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Sorption of NH_3 on Montmorillonitic Clay

I. CORNET*

(Received March 8, 1943)

Various dry minerals were permitted to react with anhydrous ammonia under controlled conditions. When the pressures of ammonia prevailing in the sorbing system were plotted against the quantity of ammonia sorbed, typically parabolic or hyperbolic sorption isotherms were obtained with ammonium bentonite, potassium bentonite, and finely ground hydrogen bentonite. Unground hydrogen bentonite gave a complex ammonia sorption curve, in which there was a short parabolic section initially, followed by an inflection and finally a second parabolic or hyperbolic sorption section. Concurrent x-ray studies indicated that the inflection and subsequent portion of the sorption curve were accompanied by widening of the c axis spacing. The sorption and concomitant x-ray data permitted the view that the sorption of ammonia by unground hydrogen montmorillonite occurred on exterior planar surfaces, interplanar surfaces, broken bonds, corners, and edges. Data on the thermal decomposition of ammonium bentonite were consistent with this view. It was found that sorbed ammonia occupied base exchange reactive spots; physical trapping of ammonia molecules in the interplanes would not account for the lattice expansion. The data also appeared consistent with the theory that both lattice hydroxyl ions and polarization of water molecules may give rise to base exchange capacity on grinding some clay minerals.

INTRODUCTION

THE clay mineral montmorillonite has a layer lattice (Fig. 1) which in chemical composition and crystal structure is similar to pyrophyllite; the crystal structure Pauling proposed for pyrophyllite[1] has been assigned to montmorillonite with but few modifications by Hofmann,[2,3] Marshall,[4] and others. Montmorillonite differs markedly from pyrophyllite in that it possesses high base exchange capacity† and a variable crystal spacing along the c axis.

Many investigators have studied the locus of base exchange reactions in clay minerals and have speculated on the nature of this locus. In order to be exchangeable[5] an ion must be held to the clay particle by a comparatively weak attractive force. Also, in order to be replaceable, an ion must be present on the exposed surface of a solid particle, either on the superficial surface[5–7] or on some internal channel surface.[4,8–12]

* Contribution from the Division of Soils, University of California, Berkeley, California. The author is indebted to Professor Hans Jenny for his suggestions and interest during the course of the investigation. Thanks are also due to Drs. Stout and Overstreet and to Mr. McCready for assistance in the construction of the apparatus and the purification of NH_3.

[1] L. Pauling, Proc. Nat. Acad. Sci. **16**, 123–129 (1930).

[2] Ulrich Hofmann, Kurd Endell, and Diederich Wilm, Zeits. f. Krist. **86**, 340–8 (1933).

[3] Ulrich Hofmann, Kurd Endell, and Diederich Wilm, Zeits. f. angew. Chemie **47**, 539–47 (1934).

[4] C. E. Marshall, Zeits. f. Krist. **91**, 433–49 (1935).

† Base exchange capacity is the quantity of ammonium ions a material will retain on leaching with neutral normal ammonium acetate; it is usually expressed as milliequivalents per hundred grams of oven dry colloid.

[5] W. P. Kelley, Am. Assoc. Pet. Geol. 454–465 (1939).

[6] W. P. Kelley, and Hans Jenny, Soil Sci. **41**, 367–382 (1936).

[7] U. Hofman, K. Endell, and W. Bilke, Zeits. f. Elektrochemie **41**, 469–471 (1935).

[8] C. E. Marshall, Proc. Soil Sci. Soc. Am. **1**, 23–31 (1936).

[9] C. E. Marshall, J. Soc. Chem. Ind. (London) **54**, 393–8T (1935).

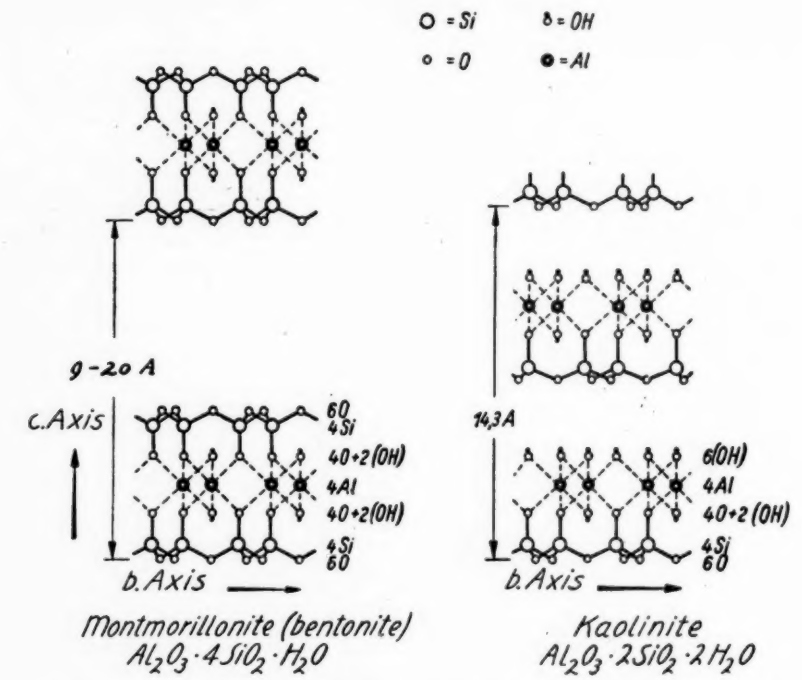

FIG. 1. Crystal structure of montmorillonite and kaolinite. The lattice dimensions are correct, but the ion sizes are not drawn to scale. (After Hofmann, Endell, and Wilm, reference 2.)

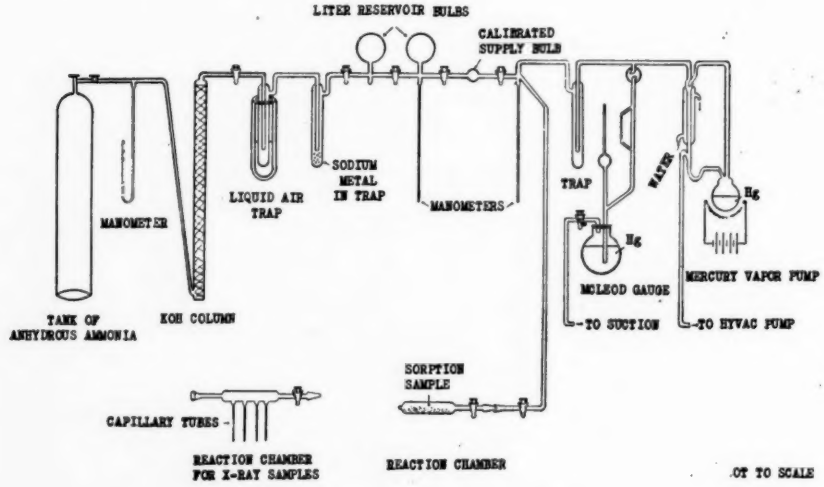

FIG. 2. The sorption apparatus.

Following a suggestion made by Professor Hans Jenny, increments of anhydrous ammonia gas were permitted to react with dry hydrogen montmorillonite and with other clays, and the lattice spacing during the course of the sorption was observed by x-rays.

EXPERIMENTAL PROCEDURE

An apparatus (shown in Fig. 2) was designed to supply anhydrous ammonia in known quantities to a reaction chamber in which dried sor-

[10] U. Hofmann and W. Bilke, Kolloid Zeits. **77**, 238–251 (1936).
[11] Ralph E. Grim, *Properties of Clay*, State Geological Survey Circular No. 49 Urbana, Illinois, 466–495 (1939).
[12] Ralph E. Grim, J. Am. Ceram. Soc. [5] **22**, 141–151 (1939).

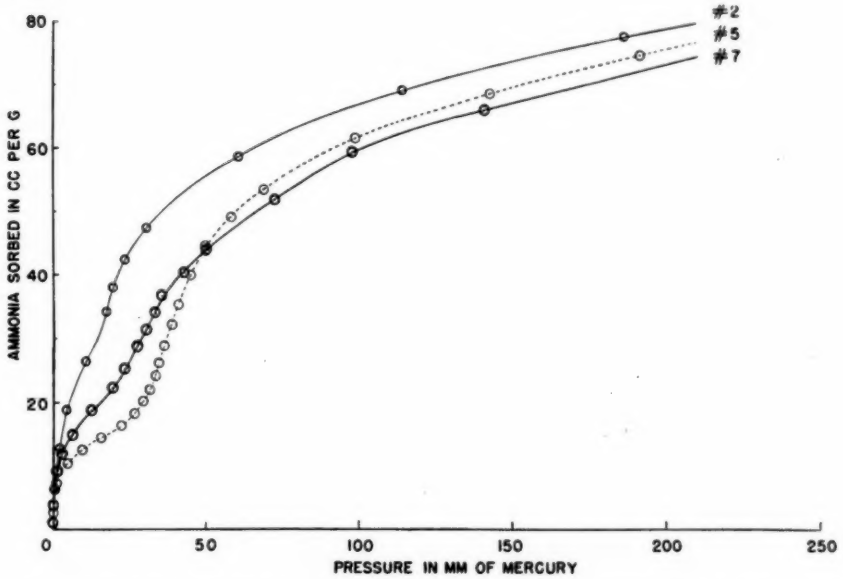

FIG. 3. Sorption of anhydrous ammonia by various hydrogen bentonites. In this and in subsequent graphs, the sorption curves refer to the sorption of anhydrous ammonia gas by one gram of colloid dried at 100°C. The quantities of ammonia gas sorbed are given in cc at normal conditions, 0°C and 760-mm pressure.

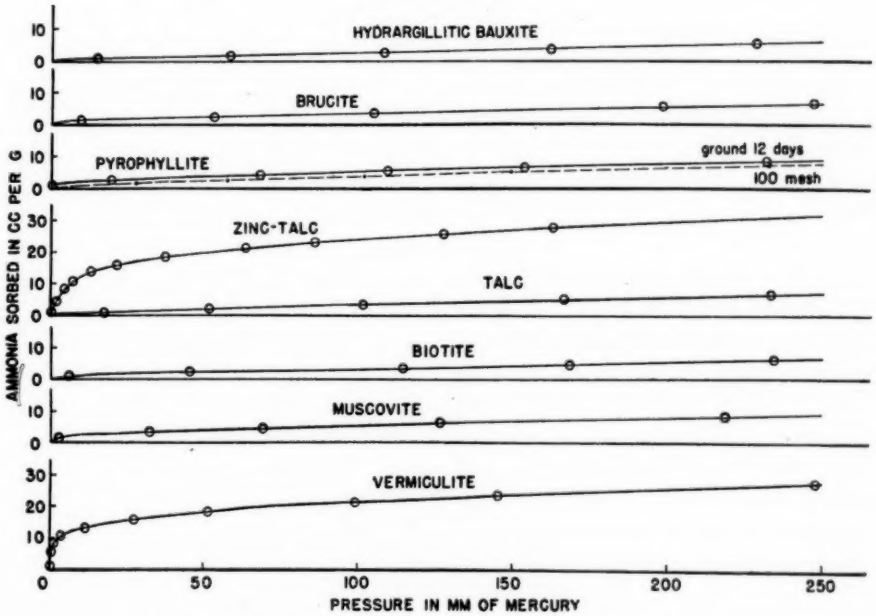

FIG. 4. Sorption of anhydrous ammonia by various minerals.

bents were placed. Manometers made it possible to follow pressure changes within the system during the course of the sorption of ammonia.

The sorption sample in the reaction chamber was brought to room temperature, and increments of ammonia were added. Two minutes after an increment of ammonia was introduced into the reaction chamber, the pressure was read. The arbitrary two-minute time interval was selected because it was not found feasible to secure all measurements at equilibrium or at a particular degree of saturation of the clay as the

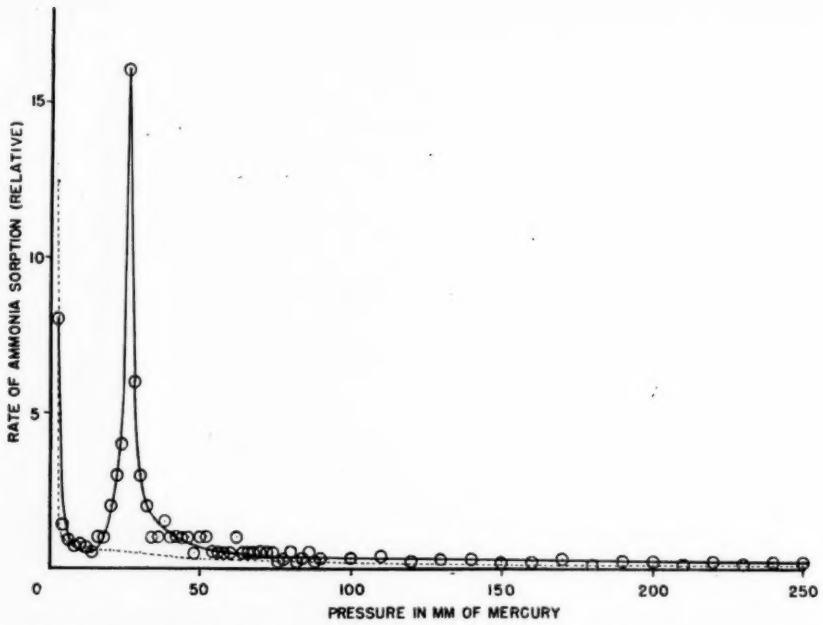

FIG. 5. Relative rate of sorption of anhydrous ammonia by hydrogen bentonite. Solid line, unground; dashed line, finely ground hydrogen bentonite. The rate of ammonia sorption is given in cc per g per 2-mm rise in pressure. This and subsequent figures refer to Wyoming type bentonite No. 3, similar to the colloid studied by Jenny, Kelley, and Brown, reference 15.

rate of saturation was a function of the degree of saturation of the sorbing clay, and at higher ammonia pressures, equilibrium was approached relatively slowly.

Of the clays used, bentonite, a relatively[13, 14] pure natural deposit, was used as a source of montmorillonite. The Wyoming type bentonite studied was similar to bentonite No. 3 used by Kelley, Jenny, and Brown.[15] Hydrogen bentonite was prepared by electrodialysis. Finely ground hydrogen bentonite which gave no pattern with x-rays was obtained by grinding hydrogen bentonite in air for twelve days in a porcelain ball mill with agate balls. Potassium-hydrogen bentonite was prepared by leaching hydrogen bentonite with normal potassium acetate, adjusted to *p*H7.

As is indicated in Fig. 2, the sorption of ammonia by a clay was carried out in a reaction chamber to which were sealed long capillary tubes. At various periods during the reaction, the capillary tubes were filled with the reaction products and cut off with an oxygen-gas torch. Thus it was possible to obtain samples at known pressures of ammonia, and with known quantities of ammonia sorbed. At no time was moisture permitted to enter the system. X-ray diffraction patterns of the samples prepared in this experiment were obtained with molybdenum $K\alpha$ radiation. From measurements of the patterns, interplanar spacings corresponding to the wide spacing or (001) line were recorded. The *hko* lines were observed, but no significant changes in position were noted.

TABLE I. The change in (001) spacing of hydrogen bentonite exposed to increasing pressures of ammonia *ca.* 25°C.

Pressure of NH_3 mm of mercury	Quantity of ammonia sorbed cc per g	meq/g	Exchange capacities	(001) Spacing A	Intensity and character of line
0 (initial)	0	0	0	9.9	vs, sharp, distinct
0	2.2	.098	.113	9.9	vs, sharp, distinct
0	2.45	.109	.126	9.9	vs, sharp, distinct
0.9	6.4	.286	.33	9.9	vs, sharp, distinct
2.0	8.0	.357	.412	9.9	vs, some broadening
5.0	10.0	.447	.515	10.0	vs, line broadening
12.0	12.5	.558	.645	10.0	s, line broadening
21.6	19.6	.875	1.01	10.0–12.5	m, diffuse, broad band
129.	75.2	3.36	3.87	12.5	vs, sharp, distinct
216.	84.0	3.75	4.33	13.5	vs, sharp, distinct

[13] John W. Gruner, Am. Mineral. **25**, 587–90 (1940).
[14] John W. Gruner, Econ. Geol. **35**, 867–75 (1940).
[15] W. P. Kelley, Hans Jenny, and S. M. Brown, Soil Sci. **41**, 259–274 (1936).

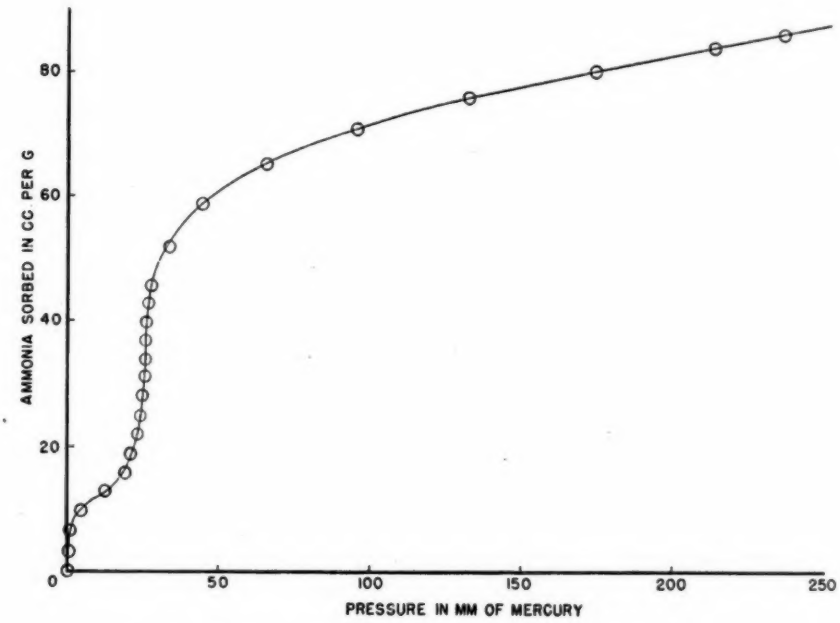

FIG. 6. Sorption of anhydrous ammonia by hydrogen bentonite.

RELATION BETWEEN SORPTION OF NH_3 AND BASE EXCHANGE CAPACITY

Dry hydrogen bentonite was permitted to react with anhydrous ammonia and the pressure of ammonia prevailing in the sorbing system was plotted against the quantity of ammonia sorbed. A complex sorption curve was obtained, in which there was a short parabolic section initially, followed by an inflection and finally a second parabolic or hyperbolic sorption section. While similar curves were obtained with several hydrogen montmorillonites (Fig. 3), no such curves were obtained for the other minerals studied. Hydrargillitic bauxite, brucite, pyrophyllite, talc, biotite, muscovite, hydrated halloysite, and other minerals investigated (Fig. 4) gave typically parabolic or hyperbolic sorption isotherms. X-ray studies were made concurrent with the course of sorption of ammonia by hydrogen bentonite. The inflection and second section of the ammonia sorption curve were found to be accompanied by widening of the *c* axis spacing. The data on the change in (001) spacing with increasing ammonia pressure are presented in Table I. The ammonium bentonite prepared from hydrogen bentonite by exposure to over 200 millimeters pressure of ammonia and subsequent evacuation at 100°C gave an (001) spacing of 11.0A, the diffraction line being strong and distinct; this ammonium bentonite had 80.8 milliequivalents of ammonia per hundred grams dry bentonite.

The sorption data and concurrent x-ray studies indicate that the unique ammonia sorption curve obtained with hydrogen montmorillonite is related to the property of expansion of the montmorillonite lattice. To verify this, finely ground hydrogen bentonite, which gave no crystal pattern with x-rays, was permitted to sorb ammonia. The sorption curve obtained was of the simple hyperbolic or parabolic type so common for the sorption of gases by fine solids. For comparison, the relative rates of sorption of ammonia by hydrogen bentonite and by finely ground hydrogen bentonite are plotted in Fig. 5. Figure 6 shows the integral sorption curve of the unground hydrogen bentonite which furnished the unique differential sorption curve of Fig. 5.

Upon evacuation of the excess ammonia from a hydrogen bentonite-ammonia system, some of the gas is retained by the colloid. It is found that this amount of NH_3 retained corresponds to the exchange capacity of the acid clay. It is believed that NH_3 reacted with the H ions of the clay

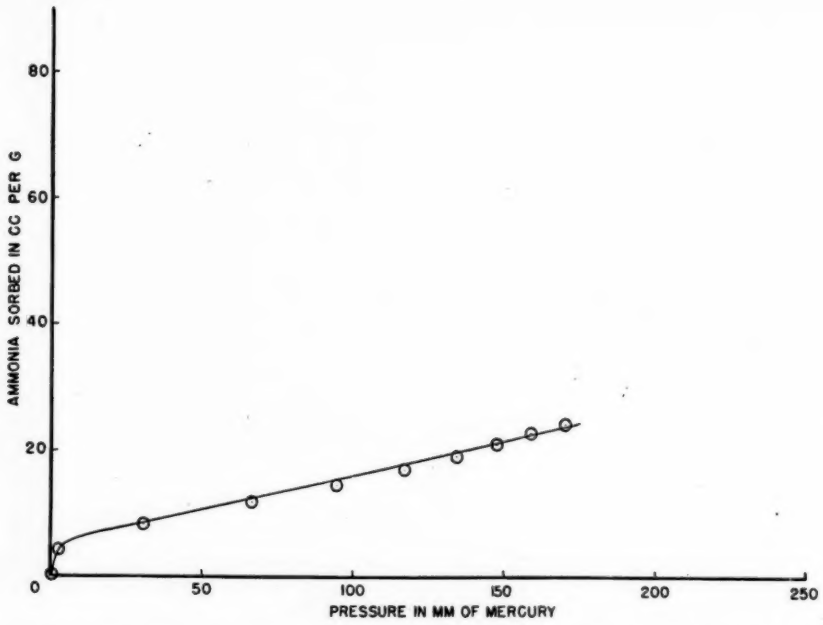

FIG. 7. Sorption of anhydrous ammonia by potassium bentonite. The low sorption capacity is associated with a lack of lattice expansion.

according to the following equation:

$$\text{CLAY} \begin{matrix}\rceil \\ \text{O} \\ \rfloor\end{matrix} - \text{H} + \text{NH}_3 \rightarrow \text{CLAY} \begin{matrix}\rceil \\ \text{O} \\ \rfloor\end{matrix} - \text{NH}_4.$$

More direct evidence that the sorbed ammonia occupies positions active in cation exchange was obtained by permitting potassium-hydrogen bentonite to sorb ammonia (Fig. 7). The partially unsaturated potassium bentonite had an (001) spacing of 10.4A, which did not change on exposure to ammonia, though 14 milliequivalents of ammonia were retained upon evacuating the sample. A comparison of the ammonia sorption of hydrogen bentonite and potassium bentonite (Table II) suggests that the ammonia retained after evacuation occupies base exchange spots.

THE SORPTION OF AMMONIA ON INTERPLANAR SURFACES

The experimental evidence (Figs. 5 and 6) indicates that when small quantities of anhydrous ammonia gas are permitted to come in contact with dry hydrogen bentonite, the ammonia is sorbed and strongly held. As more ammonia is admitted, a smaller proportion of the ammonia is sorbed, and the ammonia pressure rises. When the ammonia gas attains a pressure between 23 and 27 millimeters of mercury, a great change occurs. The ammonia is continuously sorbed in large quantities with but small change in pressure. At the end of this stage, the ammonia is sorbed continuously in the fashion so commonly found in Freundlich and in Langmuir sorption isotherms.

The x-ray patterns show distinct (001) spacings for hydrogen bentonite that had been dried at 100°C. Small quantities of ammonia, if admitted slowly, are sorbed without changing the x-ray pattern. With larger quantities of ammonia, or more rapid admission of the gas, the lattice expands. The line which characterizes the (001) spacing grows broad and diffuse. In some samples at this stage there is no (001) line and

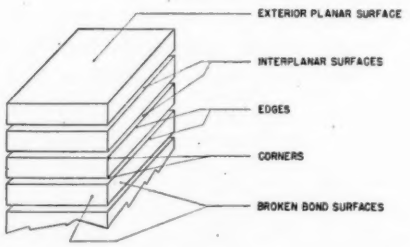

FIG. 8. Diagrammatic representation of montmorillonite clay plates.

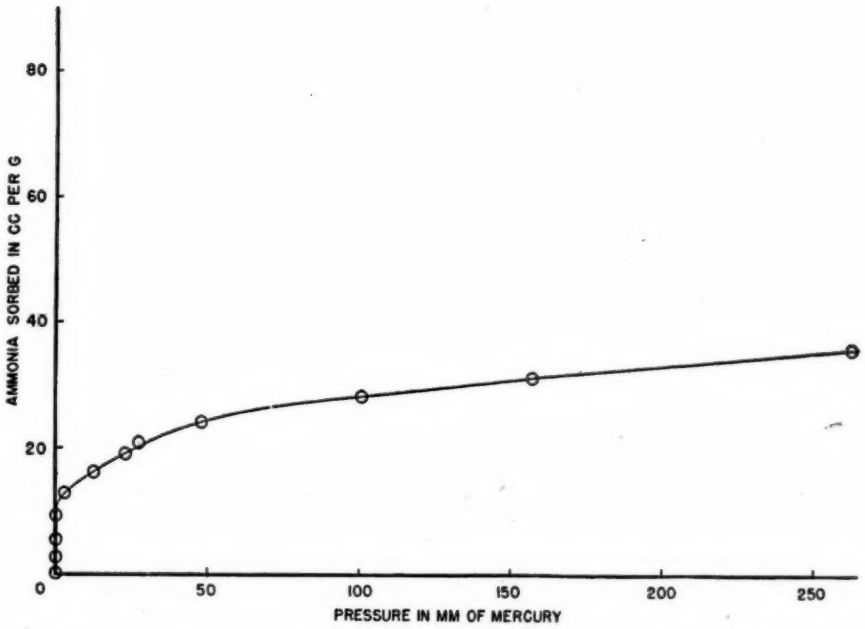

FIG. 9. Sorption of anhydrous ammonia by finely ground hydrogen bentonite. The colloid was dried at 100°C before grinding in a dry ball mill. In comparing the corresponding curve of the unground hydrogen bentonite of Fig. 6, note the decrease in sorption capacity as a result of grinding.

the sample appears to be amorphous. At about 23 millimeters pressure of ammonia, the (001) lines indicate wider spacings, showing that the montmorillonite planes are separating. From this stage on, sharp distinct (001) spacings, generally greater than 12A, are observed. Thereafter the lattice expands fairly regularly; as the ammonia pressure increases, the (001) spacing widens. It appears that reorientation of the packets has occurred. It may be recalled that P. R. Stout observed similar loss of x-ray pattern and subsequent reorientation in his study of the fixation of phosphate ion by kaolinite and halloysite.[16]

TABLE II. Comparison of ammonia sorption of hydrogen bentonite and potassium bentonite.

	Hydrogen bentonite		Potassium bentonite
The (001) spacing of the 100°C dry sample initially is	9.8A		10.4A
When exposed to dry NH_3 at a pressure of:	129 mm	216 mm	154 mm
the (001) spacing becomes:	12.5A	13.5A	10.6A
Subsequently evacuated at 100°C, the bentonites retain ammonia, the amounts retained per 100 grams of bentonite being:	80.8 meq.		14.2 meq.
In these evacuated samples, the (001) spacings are:	11.0A		10.4A

The x-ray data may be logically correlated with the peculiarities of the sorption-pressure curve. The early increments of ammonia appear to react with exterior planar and broken-bond surfaces (for a diagrammatic representation of the different surfaces of the montmorillonite lattice, see Fig. 8); these early increments of ammonia may be able to force apart some of the montmorillonite packets, as evidenced by a slight expansion of the lattice coupled with broadening of the (001) line. When these reactive surfaces are saturated, the ammonia pressure rises. At about 23 millimeters pressure, the montmorillonite packets are forced apart. At this stage, the greater the quantity of ammonia added, the more ammonia appears to go between the planes, where it probably reacts with H ions, thus maintaining the pressure constant. Further sorption of ammonia follows the customary Freundlich isothermal pattern. The x-ray pictures from this region on give clear sharp (001) lines.

[16] P. R. Stout; Proc. Soil Sci. Soc. Am. **4**, 177–182 (1939).

A finely ground bentonite shows an entirely different sorption pattern (Fig. 9). The sorption of ammonia on the ground bentonite increases continuously as the pressure rises, but the inflection which represents the separation of the packets of unground montmorillonite (Figs. 5 and 6) has disappeared on grinding. The finely ground clay gives no crystal pattern with x-rays indicating that the montmorillonite packets are disrupted and broken, and the interplanar surfaces are diminished or destroyed.[17]

Comparing Fig. 6 and Fig. 9, it may be noted that at ammonia pressures above 20 mm of mercury and within the pressure range of this experiment, finely ground dry hydrogen bentonite possesses less ammonia sorption capacity than the corresponding unground hydrogen bentonite. Finely grinding the dry clay destroys the orientation of the montmorillonite packets, and thus may eliminate the capillary condensation or polymolecular orientation of the NH_3 on the interplanar surfaces. This may explain the unique decrease in sorption of ammonia with change in surface area of the clay on fine grinding. When the excess ammonia was pumped off at a pressure of 4×10^{-5} mm of mercury at 100°C, the unground hydrogen bentonite of Fig. 6 retained 0.808 milliequivalent per gram; the corresponding finely ground hydrogen bentonite of Fig. 9 retained only 0.510 milliequivalent of ammonia per gram of clay. This decrease in retention of ammonia on finely grinding dry hydrogen bentonite is believed to indicate disruption of some of the lattice tetrahedra and octahedra in which substitutions have occurred.

Exposed *a–b* surfaces as well as interplanar *a–b* surfaces may participate in ammonia sorption and base exchange. Calculations indicate that ammonium ion may be seated in the pocket formed by the six-oxygen-ion ring of the montmorillonite lattice. The difference in expansion of the ammonium bentonite and potassium bentonite lattices during ammonia sorption could be attributed to the formation of hydrogen bonds between the interplanar NH_4^+ and NH_3 gas. Also, from the data on the sorption of ammonia by a slightly unsaturated potassium bentonite (Table II) it may be concluded that ammonia sorbed on corners and edges cannot keep the montmorillonite packets apart.

TABLE III. Retention of ammonia by clays initially ammonia saturated.

	Kaolinite				
	Unground		Ground		
Evacuated at	25°	100°	25°	100°C	
Retained	20.3	10.2	38.2	11.4	milliequivalents per 100 grams clay
	Hydrogen bentonite				
	Unground		Ground		
Evacuated at	25°	100°	25°	100°C	
Retained	92.0	87.0	112.0	81.0	milliequivalents per 100 grams clay

THE SORPTION OF AMMONIA ON BROKEN-BOND SURFACES, CORNERS, AND EDGES

Since montmorillonite has an expanding lattice, separating the packets by mechanical means would not increase the accessible planar surfaces. On the other hand, mechanical grinding might increase edges, corners, and broken-bond surfaces. Since bentonite is an impure source of montmorillonite, there may be non-expanding pyrophyllite-like lattices present and these on grinding might show an increase in accessible planar surfaces. A Wyoming type hydrogen bentonite, which had a base-exchange capacity of 80 milliequivalents per 100 grams of dry bentonite, was ground five days, and was then amorphous to x-rays. This ground bentonite was exposed to air and atmospheric moisture during a period of two years. An aliquot of this ground bentonite was dried at 100°C. On exposure to dry ammonia and subsequent evacuation at 100°C, this particular hydrogen bentonite was found to retain 96 milliequivalents of NH_3 per 100 grams of dry bentonite. If the occurrence of non-expanding pyrophyllite-like lattices in bentonite be discounted, it may be concluded that ammonia sorption and base exchange spots occur on broken-bond surfaces, edges, or corners. Kelley and Jenny demonstrated this in their study on the relation of crystal structure to base exchange,[17] using aqueous media.

THE NATURE OF REACTIVE SPOTS

For purposes of comparison, studies were made of the ammonia sorption of kaolinite (Table III). It was found that air-ground dried kaolinite

[17] G. L. Clark, *Applied X-Rays* (McGraw-Hill Book Company, New York, 1932), second edition, page 336.

showed an increase in NH_3 sorption, and again it was found that the increased ammonia sorption which arises on broken-bond surfaces was quite unstable to heat. The data also appeared consistent with the theory that the hydroxyl ions of the kaolinitic lattice can give rise to ammonia sorption and to exchange capacity when the kaolinite is ground.

The exchange capacity of the kaolinite in the experiment probably has its source in the hydroxyl ions of the broken-bond surfaces of the lattice. In montmorillonitic lattices exchange capacity may arise not only from lattice and broken-bond hydroxyl ions, but also from substitutions of ions within the tetrahedra and octahedra of the lattice. While the interpretation of the data may be less definite than in the experiment with kaolinite, the sorption of ammonia gas by ground and unground hydrogen bentonite (Table III) may indicate the nature of some of the reactive spots in montmorillonitic clays.

A hydrogen bentonite was found to increase in ammonia sorption capacity at room temperature on fine grinding, but on heating to 100°C this hydrogen bentonite was observed to have decreased ammonia retention. Since the finely ground hydrogen bentonite shows increased exchange capacity in aqueous media, it is believed that in montmorillonitic clays the polarization of water molecules on the lattice surfaces contributes to the exchange capacity.

THERMAL DECOMPOSITION OF AMMONIUM BENTONITE

The view that ammonia is held to hydrogen bentonite at different locations in the crystal lattice, and with different tenacities at the various locations, raised the question of determining the relative quantities of ammonia at the various locations. The methods used by Kelley and Jenny in their study of "The Hydration of Minerals and Soil Colloids in Relation to Crystal Structure" [15] are applicable to the thermal study of ammonium compounds. Hydrogen bentonite was suspended in distilled water and neutralized with dilute ammonium hydroxide solution. One aliquot of ammonium bentonite thus prepared was air dried for study at room temperature, the remainder was dried at 100°C and then ground to pass through a 100-mesh sieve. One-gram

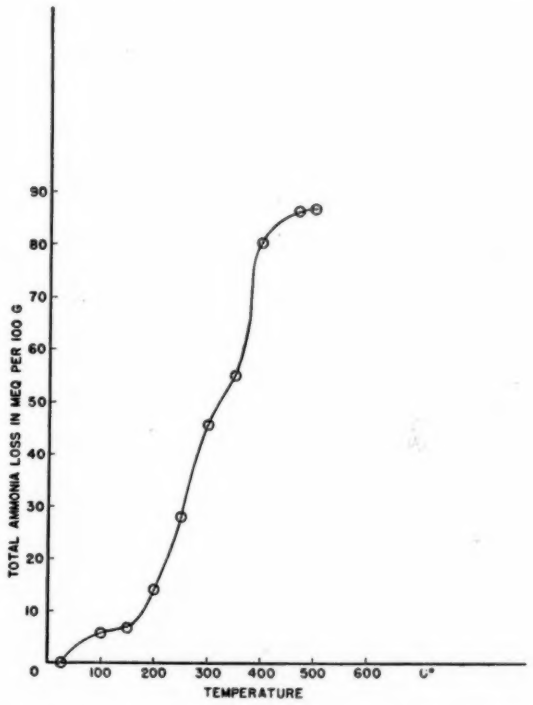

FIG. 10. Thermal decomposition of ammonium bentonite.

aliquots were heated to various temperatures and the ammonia remaining determined by distillation with MgO, trapping the liberated NH_3 in sulfuric acid, and titrating to *p*H5. At each temperature data were obtained on the quantity of ammonia lost and on the corresponding (001) spacing. The data are presented in Fig. 10. When the relative rate of ammonia loss is plotted against temperature (as shown in Fig. 11), a curve is obtained which shows peaks at 50°, 275°, and 400°C. The thermal decomposition curve indicates that ammonia is held to the montmorillonite lattice with different tenacities. About 6.5 percent of the total quantity of ammonia which the bentonite contains may be driven off by heating to 125°C. It is believed that this loosely held ammonia is bound to broken-bond surfaces. The remainder of the ammonia is rather strongly held. Work is probably required to separate the lattice planes to permit the liberation of NH_3 molecules from the NH_4 ions on the interplanar surfaces. Therefore, the earlier peak, at 275°C, is considered to represent the maximum of evolution of ammonia of the exterior planar surfaces; the peak at 400°C is thought to

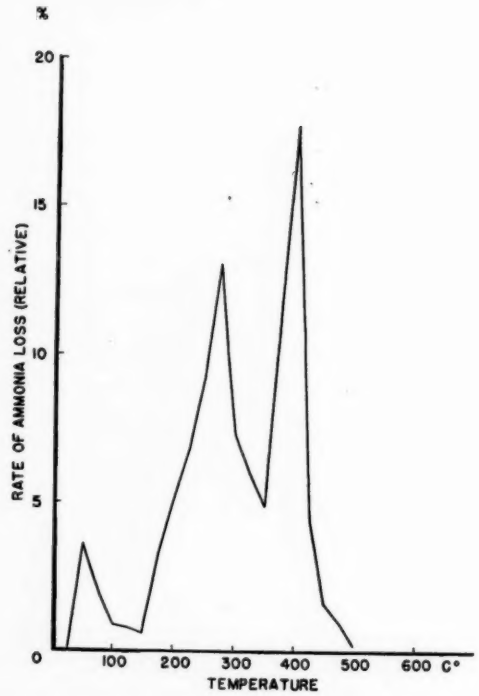

FIG. 11. Relative rate of ammonia loss with increasing temperature. The rate is given as the percent of the total ammonia of the original ammonium bentonite which is lost between two successive temperatures, as found at the higher temperature.

represent the maximum of evolution of ammonia from interplanar surfaces. Differences in composition of the ion polyhedra to which the NH_4 ion is attached may also account for the peaks. These conclusions are independent of the sorption and x-ray evidence. Hydrogen bentonite dried at 100°C has an (001) spacing of 9.83A; an ammonium bentonite must be heated to 400°C before the lattice shrinks to 9.84A, and at that stage only about 7 percent of the original ammonia remains. The x-ray data are again consistent with the view that ammonia is most strongly held to the hydrogen montmorillonite lattice on interplanar surfaces.

Bottini studied the thermal decomposition of ammonium permutite, ammonium bentonite, and ammonium clay.[18,19] From his data[18] a Geisenheim bentonite may be classified and compared with the Wyoming bentonite used in the present study. The exchange capacities of the ammonium bentonites in milliequivalents per 100 grams of colloid are 81.30 for the Geisenheim type and 86.7 for the Wyoming type.

An estimate of the distribution of ammonia upon the lattice surfaces of the two bentonites shows:

	Geisenheim bentonite	Wyoming bentonite
Broken bond	12 percent	8 percent
Exterior planar	34	55
Interplanar	54	37

The above estimates appear to be consistent with the electron microscope studies of Ardenne, Endell, and Hofmann;[20] they reported that the Geisenheim bentonite contained smaller, rougher, less platy particles than the Wyoming bentonite.

The distribution of ammonia sorption and base exchange reactive spots upon the lattice of the montmorillonitic clay will vary with the particular clay, the nature and quantity of substitutions present in the lattice, the size distribution of the colloid particles, drying, grinding, or heating of the clay. For example, grinding of a bentonite increased broken-bond capacity from 7 percent to over 41 percent.

[18] O. Bottini, Kolloid Zeits. **78**, 68–71 (1937).
[19] O. Bottini, Kolloid Zeits. **80**, 56–59 (1937).
[20] M. v. Ardenne, K. Endell, and U. Hofmann, Ber. deut. keram. Ges. **21**, 209–27 (1940).

Raman Spectra of Hydrocarbons

II. 2-Methyl-1-Heptene and 6-Methyl-1-Heptene*

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Raman frequencies, relative intensities, and depolarization factors are listed for 2-methyl-1-heptene and 6-methyl-1-heptene. The spectrograms were made on Eastman 103-J spectroscopic plates and the intensities were obtained with the aid of a Gaertner microdensitometer. The results are compared with data obtained in a previous study of 1-octene, *cis*+*trans* 2-octene, *trans*-3-octene, and *trans*-4-octene. Polarized lines at 1643 and 3000 and depolarized (or only slightly polarized) lines at 1294, 1416, and 3078 cm^{-1} correspond to olefinic frequencies of the $XHC=CH_2$ group. When the group is $XYC=CH_2$, as for 2-methyl-1-heptene, these frequencies appear at 1653, 2978, 1303, 1414, and 3077, the depolarization factors remaining essentially unaltered. Also a line of medium intensity was observed at 1674 for 2-methyl-1-heptene; its appearance is probably due to an accidental resonance degeneracy. For the group $XHC=CHY$ (*trans*), the 1416 and 3078 cm^{-1} frequencies are absent and the three remaining frequencies occur near 1300, 1672, and 2998, the last two being polarized as for the other groups. Both of the methyl-heptenes have more strong lines below 1200 cm^{-1} than did the four octenes previously studied.

INTRODUCTION

BRANCHED chain hydrocarbons containing eight carbon atoms, such as the 2-methyl-1-heptene and 6-methyl-1-heptene concerned in the present paper, would be expected to have somewhat different spectra than straight chain hydrocarbons containing eight carbon atoms. In a previous paper,[1] the Raman spectra of six straight chain hydrocarbons, four octenes and two octynes, were reported. For 1-octene, which contained the group $XHC=CH_2$, five frequencies characteristic of the olefinic linkage were observed at 1293(94)0.88, 1415(42)0.77, 1641(134)0.15, 2999(124)0.28, and 3078(23)0.93. (The first number is the Raman frequency in cm^{-1}, the number in the parenthesis is the relative intensity, and the last number is the depolarization factor.) For *trans*-2-octene,[2] *trans*-3-octene, and *trans*-4-octene, all of which contained the group $XHC=CHY$, the 1415 and 3078 cm^{-1} frequencies did not appear, the frequency 2999 was unaltered, the 1641 frequency increased to 1672, and the 1293 cm^{-1} frequency appeared at 1300, 1303, and 1290, respectively; the depolarization factors were not significantly changed.

The 6-methyl-1-heptene likewise contains the group $XHC=CH_2$ and consequently it might be expected to have the same olefinic frequencies as 1-octene, but for the 2-methyl-1-heptene the group is $XYC=CH_2$ and it might be expected that the absence of hydrogen atoms on one of the ethylenic carbon atoms would cause appreciable changes in the olefinic frequencies. The determination of possible changes of this nature was the chief purpose of this investigation. No previous Raman data seem to have been reported for the two methyl heptenes.

EXPERIMENTAL

The apparatus and experimental technique were described in the previous paper.[1] The use of film was abandoned in the present work, all the spectrograms being made upon Eastman 103-J spectroscopic plates. The microdensitometer was calibrated by the inverse square law method previously described[1] and this calibration was subsequently checked by another method involving the use of two Nicol prisms.[3] The light source for the calibration was a small filament tungsten lamp (auto lamp) operated from three 6-volt storage batteries connected in parallel. The relative intensities of the light passing

* Presented at the New York meeting of the American Physical Society, Columbia University, January, 1943.

[1] Forrest F. Cleveland, J. Chem. Phys. **11**, 1 (1943).

[2] Supposed to be a mixture of the *cis* and *trans* isomers, but the spectrum indicated that the sample was *trans*.

[3] Cf. D. H. Rank, R. W. Scott, and M. R. Fenske, Ind. Eng. Chem. Anal. Ed. **14**, 816 (1942).

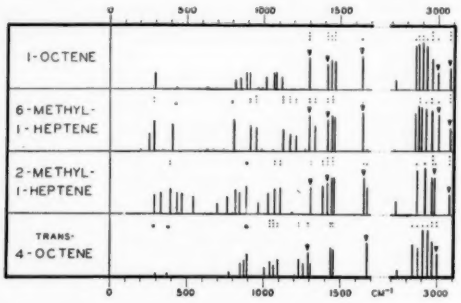

FIG. 1. Comparison of the Raman data for olefins containing the groups $XHC=CH_2$, $XYC=CH_2$, and (*trans*) $XHC=CHY$.

through the Nicol prisms at various settings were determined by use of a photovoltaic cell and galvanometer. By making one-hour exposures for various settings of the Nicol prisms it was thus possible to obtain density marks on the plate corresponding to known relative intensities. The spectrograms were made with the samples in the liquid state and excitation was, as before, exclusively by Hg 4358A.

The physical properties and a brief summary of the methods used for the preparation of the materials is as follows:

2-Methyl-1-heptene,

$CH_3(CH_2)_4(CH_3)C=CH_2$, C_8H_{16}: Prepared by condensation of methallyl chloride with butyl magnesium chloride; f. p. −90.14 °C; b. p. 119.3–119.9 °C; n_D^{20}, 1.4123; d_4^{20}, 0.7206.

6-Methyl-1-heptene,

$CH_3CH(CH_3)(CH_2)_3CH=CH_2$, C_8H_{16}: Prepared by condensation of allyl chloride with normal amyl magnesium chloride, in 60 percent yield; f.p. glass; b.p. 113.19 °C; n_D^{20}, 1.4068; d_4^{20}, 0.71195.

RESULTS

The Raman data obtained for the two methylheptenes are listed in Table I. For convenience in tabulation, the intensity values are given to the nearest whole number. This is not meant to imply, however, that all of the figures are significant. As was stated in the previous paper,[1] the error due to inaccuracy in setting the microdensitometer is about 2 percent of the reported values. In addition to this, variation in the emulsion from plate to plate undoubtedly introduces errors, probably of the order of 5 percent.[4] Furthermore, the calibration was made near the middle of the 700A range in which the Raman spectrum appears and no correction was made for variation in sensitivity of the plate in the 350A region on either side of the calibration wave-length. Hence the values of the relative intensities are to be regarded as only semi-quantitative, but they are certainly more reliable than the "estimated intensities" usually reported.

Since the depolarization factors are ratios of the intensities of two lines at the same wave-length, variation in sensitivity of the plate with wave-length and variation in the emulsion from plate to plate would cause little or no error in the values obtained for them. However, since no correction has been made for the convergence of the incident light beam, due to the cylindrical filter and Raman tubes, the depolarization factors should be regarded only as upper limits, for this convergence would tend to increase slightly the value of the depolarization factors for polarized lines.

A graphical over-view and comparison of the data for 1-octene and 6-methyl-1-heptene, which

TABLE I. Raman data for 2-methyl-1-heptene and 6-methyl-1-heptene.*

2-methyl-1-heptene			6-methyl-1-heptene			2-methyl-1-heptene			6-methyl-1-heptene		
$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ
			201	vw		1187	vw		1170	14	0.79
			255	10					1212	12	0.56
289	17		287	75	0.44				1272	vw	
329	20					1303	52	0.64	1295	212	0.45
			345	vw					1334	48	0.55
392	38	0.39	407	55	0.32	1383	69	0.64			
431	25					1414	108	0.81	1417	112	0.56
447	vw					1444	224	0.86	1443	182	0.74
466	20					1457	195		1460	176	
540	14					1653	203	0.20	1644	342	0.19
			633	vw		1674	55	*P*	1672	vw	
698	6		671	vw		2729	32		2715	vw	
760	15		740	vw					2850	318	
						2865	728	0.18			
800	vw								2871	1000	
816	38		809	93	0.21				2890	842	0.37
						2913	1000	0.27			
840	26								2919	590	0.33
889	52	0.23	912	49	0.55	2960	253	0.72	2959	476	0.60
965	7		952	38	0.86	2978	253	*P*			
1029	24		990	vw					3001	228	0.27
1070	43	0.43	1061	vw		3077	47	0.70	3079	70	0.73
1107	49	0.46	1123	30	0.87						

* $\Delta\nu$ is the Raman frequency in cm^{-1}, I is the relative intensity based upon a value of 1000 for the strongest Raman line on the plate, ρ is the depolarization factor, vw (very weak) designates lines that were too weak to measure with the microdensitometer, *P* indicates polarized lines for which the weaker component of the polarization doublet was too weak to measure with the microdensitometer, and the braces enclose lines that were not resolved on the polarization spectrograms.

[4] Cf. G. R. Harrison, J. Opt. Soc. Am. **19**, 267 (1929).

TABLE II. Comparison of the olefinic frequencies for different groups.

							$H_2C=CH_2$								
Ethylene*				1341	St.**	0.17	1619	St.	P	3009	St.	0.10	3075	—	—
							$XHC=CH_2$								
1-octene	1293	94	0.88	1415	42	0.77	1641	134	0.15	2999	124	0.28	3078	23	0.93
6-methyl-1-heptene	1295	212	0.45	1417	112	0.56	1644 1672	342 vw	0.19	3001	228	0.27	3079	70	0.73
							$XYC=CH_2$								
2-methyl-1-heptene	1303	52	0.64	1414	108	0.81	1653 1674	203 55	0.20 P	2978	253	P	3077	47	0.70
							$XHC=CHY$								
trans-2-octene	1300	40	0.64	—	—	—	1672	47	0.23	3004	37	0.34	—	—	—
trans-3-octene	1303	87	0.56	—	—	—	1672	173	0.16	2998	59	0.29	—	—	—
trans-4-octene	1290	41	0.54	—	—	—	1672	150	0.19	2997	27	0.36	—	—	—

* Data from M. Magat, *Tables Annuelles de Constantes et Données Numériques, Effet Raman* (Hermann et Cie, Paris, 1937), Vol. 12, p. 53.
** St. =strong.

contain the group $XHC=CH_2$; 2-methyl-1-heptene, which contains the group $XYC=CH_2$; and *trans*-4-octene, which contains the group $XHC=CHY$, is given in Fig. 1. The height of the line is proportional to the logarithm of the relative intensity. Polarization characteristics are indicated by single dots above the line for $\rho<0.35$, two dots for $0.35\leq\rho\leq0.65$, and triple dots for $\rho>0.65$.

DISCUSSION

Bourguel and Piaux[5] pointed out that the Raman lines near 1297 (strong), 1416 (medium), 1642 (strong), 3002 (strong), and 3080 (medium) were characteristic of straight chain olefins containing the group $XHC=CH_2$; they did not determine the polarization characteristics of the lines. The values of these five olefinic frequencies for the six olefins concerned in this and the previous investigation and the corresponding frequencies for ethylene are listed for comparison in Table II. As was expected, the frequencies for the 6-methyl-1-heptene were within experimental error of the values previously obtained for 1-octene. For 2-methyl-1-heptene, the 1416 and 3078 cm^{-1} frequencies likewise remained constant, but the 1294 and 1643 frequencies increased to 1303 and 1653, respectively, and the 3000 frequency dropped to 2978. The depolarization factors for the five methylheptene lines were not greatly different from those of the corresponding lines of the four octenes; for both, the lines near 1650 and 3000 were polarized, the others depolarized or only slightly polarized. The five olefinic frequencies are indicated by the wedge-shaped symbols in Fig. 1.

The line near 1673 cm^{-1}, of medium intensity for 2-methyl-1-heptene and of very small intensity for 6-methyl-1-heptene, might be thought to indicate the presence of some *trans* olefin as an impurity. If this were the case, however, one would also expect to observe a line near 3000 cm^{-1} in the spectrum of 2-methyl-1-heptene. Since no line of this frequency was observed, it seems more probable that the appearance of these two lines is due to an accidental resonance degeneracy, at least for 2-methyl-1-heptene.

In addition to the five frequencies discussed above, 2-methyl-1-heptene and 6-methyl-1-heptene have prominent, slightly polarized lines at 1383 and 1334 cm^{-1}, respectively, not present with comparable intensity in the spectra of the four octenes. (There was a line at 1375 for *trans*-2-octene[2] and for *trans*-3-octene, but their intensities were not comparable to that of the two lines in question.) The two methylheptenes also are distinguished from the other octenes by the presence of a prominent, polarized line near 400 cm^{-1} and both compounds have more strong lines

[5] M. Bourguel and L. Piaux, Bull. Soc. Chim. 2, 1958 (1935).

below 1200 cm^{-1} than did the previously studied octenes. For 6-methyl-1-heptene a group of three lines at 1123, 1170, and 1212, not present in the spectra of the other five olefins, is outstanding. A group of three lines with comparable separations and intensities appears at 1029, 1070, and 1107 for the 2-methyl-1-heptene; this compound also yields five relatively strong lines in the 430–800 cm^{-1} region where no strong lines were observed for the other five olefins. Lines below 1200 cm^{-1} which have nearly constant frequencies in the six spectra are the ones near 290 (weak, slightly polarized) and 1065 (weak, depolarized or only slightly polarized). Lines near 840 and 875 cm^{-1} were observed for all except 6-methyl-1-heptene.

ACKNOWLEDGMENTS

The hydrocarbons used in this work were prepared under the direction of Professor C. E. Boord of the Department of Chemistry of the Ohio State University as part of the American Petroleum Institute Hydrocarbon Research Project in the Industrial Research Foundation of the University. The microdensitometer used in the intensity measurements was obtained with a grant made to the author from the Penrose Fund of the American Philosophical Society. The Hilger spectrograph was obtained, in part, with a grant made to the author from the Permanent Science Fund of the American Academy of Arts and Sciences. The author wishes to express his appreciation for this assistance.

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Infra-Red and Raman Spectra of Polyatomic Molecules

XIX. Acetaldehyde and Acetaldehyde-d_4

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The infra-red spectra of acetaldehyde and acetaldehyde-d_4 have been measured between 3μ and 25μ. An analysis of the spectra has been made and values are suggested for the fundamental vibration frequencies of these molecules. These values are compared with the assignment for the propylene molecule, and a strong similarity is shown. The results have been used to calculate the height of the potential barrier restricting internal rotation in acetaldehyde, and a value of about 2000 cal. is deduced.

THE molecule of acetaldehyde is an interesting one from the viewpoint of hindered internal rotation since it involves the rotation of a group with substituents at 120° angles against one with substituents at 180° angles. Thus at any of the symmetrical positions there are always some atoms in an opposed position and some of the rotating atoms in a staggered configuration. This might result in a leveling of the restricting potential, or, if there were a strong attraction between the methyl hydrogens and the oxygen atom in the same molecule, might result in a considerable enhancement of the restricting potential. The other studied molecules which exhibit this same phenomenon, acetone[1] and propylene,[2] both show potential barriers somewhat smaller than that found for other molecules, and that for acetone is very low.

As a contribution to the determination of the fundamental properties of the acetaldehyde molecule, the infra-red spectra of acetaldehyde and acetaldehyde-d_4 have been measured, and an attempt has been made to fix their fundamental frequencies.

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[1] S. C. Schumann and J. G. Aston, J. Chem. Phys. **6**, 485 (1938).
[2] B. L. Crawford, Jr., G. B. Kistiakowsky, W. W. Rice, A. J. Wells, and E. B. Wilson, Jr., J. Am. Chem. Soc. **61**, 2980 (1939).

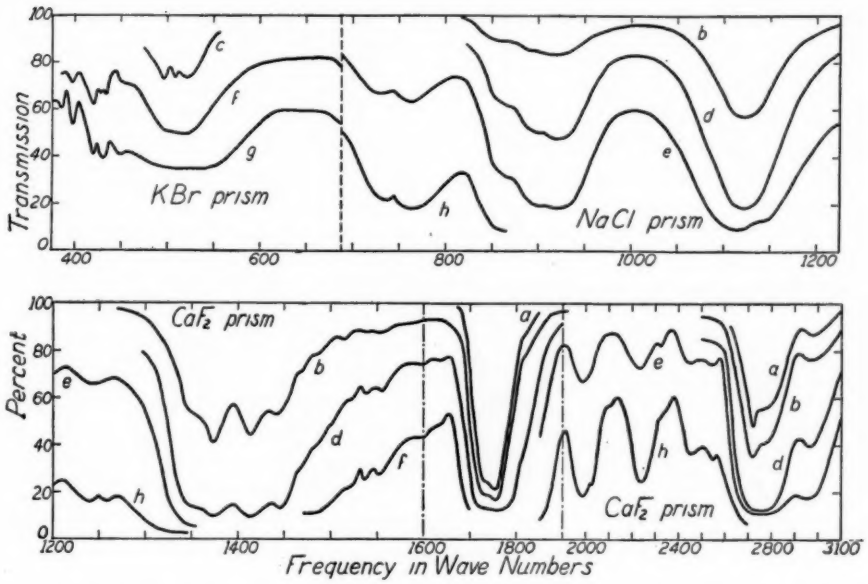

FIG. 1. Infra-red spectrum of acetaldehyde. Gas pressures for various curves in mm of Hg: (a) — 8; (b) — 14; (c) — 25; (d) — 50; (e) — 150; (f) — 200; (g) — 700; (h) — 750.

EXPERIMENTAL PART

The spectra were obtained on the instrument described in previous communications from the Harvard laboratories[3] improved as described in the latter paper. The gas was contained in cells 30 cm in length and 4 cm in diameter, with plane rocksalt or KBr plates sealed on at the ends with Picein or Apiezon wax, which were found resistant to the action of acetaldehyde.

The acetaldehyde used was an Eastman product which was redistilled several times in a vacuum system from an ice-bath to a bulb cooled with CO_2-ether mixture. The vapor pressure of the final product agreed with that recorded in the literature for acetaldehyde, and it was stored for over a year without appreciable polymerization.

The acetaldehyde-d_4 was prepared from C_2D_2 and D_2O by the method of Zanetti and Sickman,[4] with minor modifications. The calcium carbide used had been prepared under especially anhydrous conditions for Dr. Fred Stitt and was kindly given by him. After being placed in the reaction system, the carbide was heated to 450° in a vacuum to remove any traces of light hydrogen present as $Ca(OH)_2$. After treatment of the carbide with D_2O and absorption of the C_2D_2 in D_3PO_4 solution, the resultant mixture was fractionated several times in the vacuum system, until a water-white liquid was obtained whose vapor pressure at 0° agreed with that recorded by Zanetti and Sickman. This acetaldehyde-d_4 also remained in the monomeric form over a period of a year. That it was substantially free from light hydrogen is shown by the feebleness of any possible absorption corresponding to C—H vibrations, which allows an estimate of purity certainly better than 99 percent.

The absorption curves obtained at various pressures for the range 3μ to 25μ are shown in Figs. 1 and 2 for CH_3CHO and CD_3CDO, respectively. In Tables I and II are listed the frequencies of absorption bands as shown by these curves, together with an estimate of their intensities, and infra-red and Raman data obtained by other observers. The choice of frequencies is for the most part unambiguous except in the region 1400 to 1600 cm^{-1} for acetaldehyde where the spectrum is very complicated. Here, the groupings of the maxima observed into absorption bands is somewhat arbitrary.

[3] (a) H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 197 (1938); (b) E. B. Wilson, Jr. and A. J. Wells, J. Chem. Phys. **9**, 319 (1941).

[4] J. E. Zanetti and D. V. Sickman, J. Am. Chem. Soc. **58**, 2034 (1936).

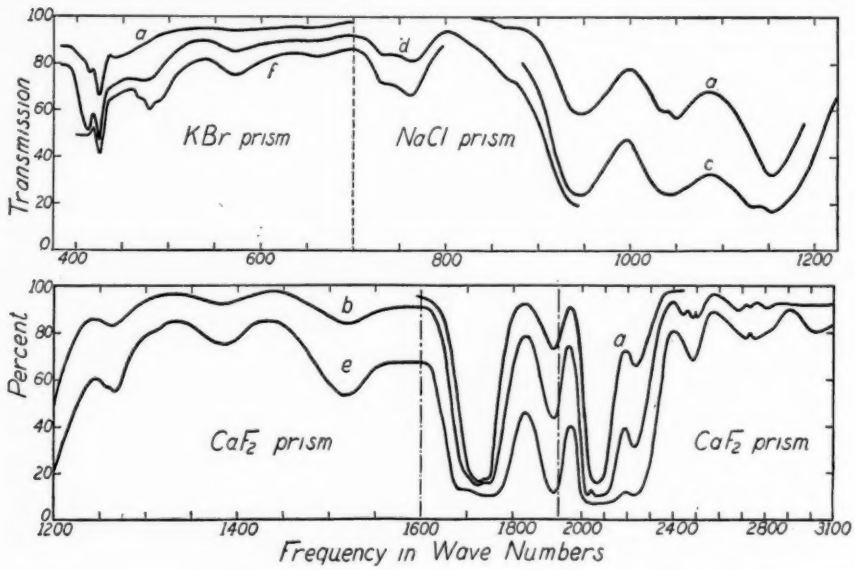

FIG. 2. Infra-red spectrum of acetaldehyde-d_4. Gas pressures for curves in mm of Hg: (a) — 30; (b) — 99; (c) — 103; (d) — 200; (e) — 335; (f) — 420.

DISCUSSION OF RESULTS

Since the completion of the experimental part of this work there has appeared a detailed study of the spectrum of acetaldehyde by Thompson and Harris.[5] The present results confirm their work in all except a few weak bands, but because this work extends their results from 20 to 25μ, and because of the intimate relation between the spectra of the light and heavy acetaldehyde, the present results have been presented in their entirety.

The infra-red spectrum of acetaldehyde has also been studied by Weniger[6] and by Gerding and LeComte.[7] Neither of these is very complete. The Raman spectrum has been the subject of a number of studies,[8] which have been quite thoroughly discussed by Thompson and Harris.[5] Since the data of Gerding and Rjinders are the most complete and since their results check some obtained in this investigation, their figures are the ones included in Table I. In addition to these results Gerding, Nijveld, and Rjinders[9] have recently published some detailed data on the polarization of the Raman lines, which are also included in Table I.

There have been no previous determinations of the infra-red spectrum of acetaldehyde-d_4, but its Raman spectrum has been studied by Wood.[10] The frequencies he listed are tabulated in the third column of Table II.

The analysis of the spectrum which follows uses substantially the same argument as that put forth by Thompson and Harris, with the exception that, because of the more complete information available as a result of the present work, it is possible to specify many of the frequencies more exactly and it is necessary to change some of the assignments.

There are fifteen normal modes of vibration in the acetaldehyde molecule, counting the restricted internal rotation. Since the symmetry of the molecule is very low—one plane of symmetry at best—all of the vibration frequencies are permitted in both the Raman and the infra-red. Of these ten will be in-plane or symmetrical with

[5] H. W. Thompson and G. P. Harris, Trans. Faraday Soc. **38**, 37 (1942).
[6] W. Weniger, Phys. Rev. **31**, 388 (1910).
[7] H. Gerding and J. LeComte, Rec. Trav. Chim. **58**, 614 (1939).
[8] (a) A. Petrikaln and J. Hochberg, Zeits. f. physik. Chemie **B4**, 299 (1929); (b) A. Dadieu and K. W. F. Kohlrausch, Wien. Ber. **138**, 607 (1929); (c) S. Venkenteswaren and S. Bhagavantam, Proc. Roy. Soc. **128A**, 252 (1930); (d) E. Canals and J. Gastaud, Bull. Soc. Chim. [5] **4**, 2042 (1937); (e) K. W. F. Kohlrausch and F. Koppl, Zeits. f. physik. Chemie **B24**, 370 (1934); (f) H. Gerding and G. W. A. Rjinders, Rec. Trav. Chim. **58**, 603 (1939).
[9] H. Gerding, W. J. Nijveld, and G. W. A. Rjinders, Rec. Trav. Chim. **60**, 25 (1941).
[10] R. W. Wood, J. Chem. Phys. **4**, 536 (1936).

the plane of symmetry and hence will be polarized in the Raman effect, while the other five will be unsymmetrical, depolarized lines. Of the ten in-plane frequencies, five are essentially parallel with the minor axis of inertia and five are approximately perpendicular to it, with the former being the more strongly polarized. This divides the frequencies into three groups as shown in Table III, where the suggested assignments are tabulated.

The assignment of the frequencies to the acetaldehyde molecule is facilitated by the fact that the molecule is very similar dynamically to the propylene molecule, except for motions within the CH_2 group, and therefore the excellent analysis of Wilson and Wells[3b] on this molecule can be used as a basis for the assignment of frequencies to acetaldehyde. Thompson and Harris have also pointed this out, but their parallelism was upset by the lack of definite information as to the existence of the band at 426 cm^{-1}. When use is made of this band the similarity becomes very pronounced.

(a) Stretching Frequencies

There will be four stretching frequencies involving the C−H bond: three for the methyl group and one involving the aldehyde group. Both CH_3CHO and CD_3CDO show three strong frequencies in the infra-red in the expected regions, and for each there is one frequency in the appropriate region observed strongly in the Raman spectrum, but not in the infra-red. These latter—2915 cm^{-1} for CH_3CHO and 2128 cm^{-1} for CD_3CDO are assigned to correspond. The others have been paired solely on the basis of similarity of combination or difference bands, but since there are not many such bands involving these frequencies, the pairing has no great significance. The assignment of the frequencies to the various groups is also arbitrary.

There is one disagreement with Thompson and Harris. They regard 2915 cm^{-1} as a combination frequency involving resonance and call 3004 cm^{-1} the fourth fundamental for acetaldehyde. This seems very unlikely since 2915 cm^{-1} is a very strong band in the Raman effect, while 3004 cm^{-1} is very weak, and the corresponding band for CD_3CDO, at 2128 cm^{-1} is a strong band.

The C=O frequency is found quite normally at about 1700 cm^{-1} for both molecules. The C−C frequency for light acetaldehyde occurs as expected at 917 cm^{-1} but the only available corresponding band for deuteroacetaldehyde is a much weaker one at 860 cm^{-1}. The reason for this marked decrease in intensity is not apparent, but nevertheless the assignment seems to be the

TABLE I. Infra-red frequencies of acetaldehyde (in cm^{-1}).

Present work	Thompson and Harris	Intensity	Raman	Polar.	Assignment
387, 398		med			917−515
421, 431		str			fundamental
450		weak			1360−917
497					
509	525	str	516	6/7	fundaemntal
523					
	(625)?*				1740−1121
733, 765	764	med	779	6/7	fundamental
852	852	med			2×426
890	883	str	894, 923	0.73	fundamental
917	918	str			fundamental
	(974)?*				1414−426
1121	1114	str	1118	0.52	fundamental
	1222*		1207(?)		1740−515
1241, 1258		med			509+760
	1295*		1307(?)		1740−426
1342, 1373	1348, 1370	v. str	1351		fundamental
1414	1405	v. str	1395	6/7	fundamental
1445	1440	v. str	1433		fundamental
1464		v. wk			
1486		v. wk			2×760
1515		v. wk			
1535, 1552	1546	weak			1121+426
1608, 1630	1600(?)	v. wk			1121+515
1732, 1755	1720, 1760	v. str	1721	0.60	fundamental
1840	1825(?)	weak			2×917
1987	1980	med			1121+890
	2012*				1121+890
2242	2222	med			2×1121
	2260*				1360+890
2325		weak			1414+917
2453	2457	weak			2970−515
2551	2551	weak			2970−426
	2688*				
2710	2704	v. str	2735		fundamental
	2732			0.45	
2788	2758, 2778	v. str	2758		fundamental
	2800		2844		2×1405
			2918	0.25	fundamental
2964	2976	str	2971		fundamental
			3004		
3424	3436	med			2×1740

* On reexamination of our absorption curves it was possible to find indications of very weak bands for all of these frequencies except the one at 625 cm^{-1}, of which there is no sign.

only possible one. The 917 cm^{-1} band is chosen for this frequency rather than the 890 cm^{-1} band, because the similarity of combination frequencies, which is rather extensive in this case, pairs the latter with the 755 cm^{-1} band in CD_3CDO. This is far too much shift to be the C—C frequency.

(b) Bending Frequencies

For these molecules there are three methyl bending frequencies, which are expected in the neighborhood of 1400 cm^{-1} for acetaldehyde and 1100 cm^{-1} for acetaldehyde-d_4. They can be accounted for by the bands at 1445, 1414, and 1370 cm^{-1} for CH_3CHO and by the maxima at 1155, 1130, and 1042 cm^{-1} in the case of CD_3CDO. Pairing these can again be accomplished on the basis of combination frequencies, which gives the results shown in Table III. For the assignment of these to specific classes the polarization data are of no value, since the lines have been grouped as a unit in that work. Consequently, the choice of Wilson and Wells for propylene has been followed, and the frequencies for acetaldehyde have been listed in corresponding order as to size.

TABLE II. Infra-red frequencies of acetaldehyde-d_4 (in cm^{-1}).

Frequencies	Intensity	Raman	Assignment
380(?)	med		860−479
400	med		1155−755
413, 425	str	422.4	fundamental
438	weak		860−420
465, 479, 490	med		fundamental
570	med		fundamental
657	v. wk		1130−479
730, 763	med	762	fundamental
860	med		fundamental
944	str		fundamental
1036, 1048	str	1024	fundamental
1130	med	1090	fundamental
1155	str	1153	fundamental
1253, 1266	med		1735−480
1317(?)	v. wk		1735−420
1386	weak		944+420 (or res. light H)
1518	med		2×755
1678	med	1692	944+755
1727, 1750	v. str	1706	fundamental
1889	med		2×944
2033	v. str		fundamental
2089	v. str	2072	fundamental
		2128	fundamental
2235	str		fundamental
2485	weak		1735+755
2710	v. wk		residual C−H
2767	v. wk		residual C−H
3012	weak		2089+944
3210	weak		2089+1130
3424	weak		2×1735

The lowest frequency in the molecule should be that corresponding to the C—C—O bending. It is located at 426 cm^{-1} for acetaldehyde and at 419 cm^{-1} for acetaldehyde-d_4.

The other bending frequency involves the aldehyde group, the actual motion being best described as a wagging of the hydrogen. Wilson and Wells assign to the corresponding frequency in propylene the value 1297 cm^{-1}. To conform with this there is a band found at 1250 cm^{-1} in the acetaldehyde spectrum. This does not seem a likely choice for a fundamental, however, the band not having been found at all by Thompson and Harris. Nor has it been reported in the Raman effect. A more probable value seems to be the 1121 cm^{-1} band in CH_3CHO to which the 944 cm^{-1} band in CD_3CDO corresponds. The 1121 cm^{-1} band is polarized in the Raman effect, as would be expected for this assignment.

(c) Rocking Frequencies

There are three of these frequencies to be accounted for—an in-plane and an out-of-plane rocking of the methyl group and an out-of-plane rocking of the aldehyde hydrogen. The first should be polarized, the latter two depolarized. For the hydrogen rocking the depolarized line at 515 cm^{-1} may be assigned in the case of acetaldehyde, with the corresponding frequency at 480 cm^{-1} for acetaldehyde-d_4. This frequency in propylene has been assigned a value of 578 cm^{-1} by Wilson and Wells. For the other rocking assignments to CH_3CHO the bands at 890 and 755 cm^{-1} are indicated, although the latter is too low according to the calculations on propylene. The corresponding CD_3CDO frequencies are 755 and 570 cm^{-1}. The 760-cm^{-1} line is depolarized, indicating that it is the out-of-plane frequency.

An alternative assignment would make 1250 cm^{-1} the hydrogen wagging frequency and locate the rocking frequencies at 1121 and 890 cm^{-1}, leaving 760 cm^{-1} as a combination or difference band. This would accord better with the assign-

ments for propylene, but seems less valid since the presence and strength of the Raman line at 760 cm^{-1} indicate that this frequency should be treated as a fundamental. It should be noted that propylene also has an unexplained frequency at 755 cm^{-1}.

This assignment accounts for all the frequencies of both light and heavy acetaldehyde except for the restricted internal rotation.

INTERNAL ROTATION IN ACETALDEHYDE

Unfortunately heat capacity data are not available which would allow the evaluation of an accurate calorimetric value for the entropy of acetaldehyde to compare with the spectroscopic value. However, it has been possible to estimate a fairly accurate value from the equilibrium and heat of the reaction

$$CH_3CHO+H_2=C_2H_5OH.$$

The heat of this reaction in the gaseous state at one atmosphere and 355°K has been determined by Kistiakowsky and co-workers[11] to be $\Delta H_{355}=-16{,}750$ cal. The equilibrium has been determined at somewhat higher temperatures by Rideal[12] and by Bancroft and George.[13] These results are in good agreement and a short extrapolation of their data gives $\Delta F_{352}=-6500$ cal. This value, combined with the figure for ΔH gives a ΔS_{352} for this reaction of -29.2 entropy units, which may quite possibly be in error by 0.5 entropy units.

The entropy of hydrogen gas at 352°K is 32.31 entropy units,[14] while that of ethyl alcohol vapor at the same temperature has been evaluated as 69.8 entropy units by Schumann and Aston.[15] Proper combination of these data leads to an experimental value for the entropy of acetaldehyde, $S_{352}=66.7$ cal./deg./mole.

For the spectroscopic calculation of the entropy the moment of inertia may be determined from the molecular dimensions given by Stevenson, Burnham, and Schomaker.[16] The product of the moments of inertia is evaluated as 29,350 with units in angstroms and in atomic weight units. By using this and the frequency assignment of this paper, the entropy of acetaldehyde as an ideal gas at 352° excluding internal rotation comes out to 63.6 entropy units. Taking the reduced moment of the rotating groups as 4.4×10^{-40} g cm^2 as given by Thompson and Harris,[5] the entropy contribution for a free internal rotation comes to 3.6 entropy units. With this and an allowance of 0.2 entropy unit for gas imperfection, the entropy of acetaldehyde at 352°, assuming free internal rotation, is calculated to be 67.4 cal./deg./mole.

The difference between this value and the experimental one, 0.7 entropy unit, corresponds to a barrier restricting internal rotation of about 2100 cal. according to the tables published by Pitzer.[17] This is in the same range as values already computed for other molecules. Although the numerical accuracy is not great enough to draw conclusions about a leveling-off of the potential barrier restricting rotation, nevertheless one can say that there is no great specific interaction tending to increase the barrier.

I am grateful to Professor E. Bright Wilson, Jr. for the use of the Harvard spectrometer, and I should like to thank both him and Dr. A. J. Wells for helpful discussions during the course of this work.

TABLE III. Frequency assignments to normal modes.

Vibration	Acetaldehyde	Acetaldehyde-d_4	Propylene*
symmetrical CH_3 stretch	2710	2033	——
symmetrical CH_3 bend	1370	1042	1399
symmetrical C−C stretch	917	860	919
C=O stretch	1740	1730	1647
wagging of C−H	1121	944	1297
unsymmetrical CH_3 stretch	2915	2128	——
C−H stretch	2788	2235	——
unsymmetrical CH_3 bend	1414	1155	1448
CH_3 rocking	890	755	?
C−C−O bending	426	419	428
unsymmetrical CH_3 stretch	2964	2089	——
unsymmetrical CH_3 bend	1445	1130	1472
CH_3 rocking	760	570	(755?)
C−H rocking	515	479	578
CH_3 torsion	?	?	?

* See reference 3(b) in text.

[11] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith, and W. E. Vaughan, J. Am. Chem. Soc. **60**, 440 (1938).
[12] Rideal, Proc. Roy. Soc. **99A**, 153 (1926).
[13] W. D. Bancroft and A. B. George, J. Phys. Chem. **35**, 2194 (1931).
[14] C. O. Davis and H. L. Johnston, J. Am. Chem. Soc. **56**, 1045 (1934).
[15] S. C. Schumann and J. G. Aston, J. Chem. Phys. **6**, 480 (1938).
[16] D. P. Stevenson, H. D. Burnham, and V. Schomaker, J. Am. Chem. Soc. **61**, 2922 (1939).
[17] K. S. Pitzer, J. Chem. Phys. **5**, 467 (1937).

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The Structure of the Protein Molecule

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A two-dimensional double layer of amino acids is postulated as the constitution of proteins in solution. From the known size of a single amino acid residue, the shape and size of a protein molecule of molecular weight class 3500 may be estimated. The denatured molecules are postulated to have a filamentous or fibrous form, characterized by the polypeptide chain. The evidence for such a postulate is reviewed.—THE EDITOR.

OUTLINE OF THE THEORY

THE corpuscular molecule of proteins in solution may be (assumed to be) constituted of a two-dimensional double layer of amino acids. Each of these two layers bears, on one of its faces, lateral hydrophobic side chains of the leucine type and on the other lateral hydrophilic side chains (arginine, aspartic acid, etc.) with polar groups. The two layers are joined by their hydrophobic faces and expose their hydrophilic faces towards the water. These layers correspond to the films that one obtains when a protein is spread on the surface of water. From the known space occupied by a single amino acid residue in a monomolecular layer, one can calculate that a single molecule of a protein of the molecular weight class 35,000 can be represented by an object of flattened form about 60A in diameter and 15A in thickness. According to the hypothesis proposed, the thickness will remain practically constant while the diameter will increase with the molecular weight.

In each of the two united films, the structure will be imposed by the arrangement of the lateral chains. These are oriented in contact with water and are disposed in a compact assemblage which possesses hexagonal symmetry and forms flat leaflets that recall the structure of soap-like substances (*des corps smectiques*). Moreover, since the lateral chains are of different nature, they constitute the equivalent in two dimensions of a mixed crystal (alloy). When the positions of amino acids of the same kind are joined, one obtains, superposed upon the hexagonal elementary network, a kind of superstructure of the same hexagonal symmetry of such a sort that the number of amino acids of the same kind surrounding an amino acid of a different kind can only be in multiples of 2 and of 3. Each layer of the molecule of the protein accordingly constitutes the smallest element of hexagonal symmetry that one can form by associating the different amino acids in variable proportions but with the choice restricted to the series of numbers $2^n \times 3^m$. One cannot withdraw an amino acid from the network, or add one, without bringing about a collapse of the structure, or at least without bringing about a new distribution of the whole number of its constituents. This might be the significance of the rule of Bergmann and Niemann and also of the integral variation in multiples of a fundamental molecular weight suggested by Svedberg.

Unlike the disposition in the corpuscular molecule, the preponderating constitutional element in the denatured molecule, as also in the keratins or collagens, may be assumed to be the polypeptide chain. The essential modification which occurs in the course of denaturation would thus be a conversion from an oriented and metastable corpuscular state into a filamentous or fibrous form. The relatively independent peptide chains are then no longer assembled in a netlike structure, but are disposed parallel to the edges of a three-dimensional network which makes up the structure of the fiber (Meyer and Mark, Astbury). Denaturation of the protein may thus

* Sometime before the total occupation of France the manuscript of this article was submitted in French to a foundation in this country, requesting its submission for publication in an American journal. The manuscript has been translated and submitted to *The Journal of Chemical Physics*.

Reviewers of the article have suggested various alterations which, under normal circumstances, would have been requested of the author. It was not felt, however, in view of the inaccessibility of the author, that the editors should accept the responsibility of making such alterations without approval of the author.—THE EDITOR

be defined as a passage into a filamentous state (*l'etat nématique*).

The notion of the protein as a flat molecule with a surface crystalline structure of which the pattern and order of arrangement vary according to the proportions of the different functional groups is of great biological significance. It not only gives a key to the conditions which were in control during the synthesis of the proteins, but also provides a hint of the mechanism of formation of antibodies and of the action of ferments which is much more reasonable than views based upon a more or less globular molecular form. By analogy with the soaps, it explains the greater part of the physico-chemical properties of either dilute or relatively concentrated solutions of protein; the x-ray diagrams, the dissymmetry coefficient of Svedberg, the products of dissociation, of hydration, swelling, and changes of phase, and of electric mobility.

There follows a review of the evidence which can be advanced in favor of this constitution of the molecule and a development of the physico-chemical consequences.

PROTEIN MONO-LAYERS

Whatever the constitution of the molecule in solution may be, it is generally admitted that, when a protein is spread on the surface of water, the molecule expands under the action of orienting forces and disposes itself in such a manner that the greatest possible number of polar groups is immersed in the water. On the other hand, non-polar lateral chains are turned towards the air.

Each amino acid residue, according to the nature of its hydrocarbon-chain, behaves, if not in an independent manner, at least in one that is autonomous. Inasmuch as all proteins are composed of amino acids of which the average molecular weight is within narrow limits the same, the surface concentration in the monolayers of different proteins should also be practically the same and be independent of the molecular weight. With regard to the constancy of the thickness, or more exactly, of the surface concentration, there is some controversy which arises for the most part from the fact that spreading experiments have not always been carried out under ideal conditions.

The layer has often been formed without the precaution of starting with crystalline material. Furthermore it has been shown[1–3] that, in order to spread solid protein most perfectly, it is necessary that, during the formation of the layer, the pressure shall at no moment exceed a few tenths of a dyne. Monolayers under greater pressure possess a greater concentration, are not stable, exhibit an aging effect and have a viscosity limit much too large. Moreover these thick monolayers change very slowly towards a stable state as soon as the pressure is reduced below 1.5 dyne.

During a systematic study of the spreading of gliadin from alcohol solution, Mitchell[4] has shown that, in order to obtain complete spreading of the protein, the concentration in the drop placed on the surface should be less than a maximum value of about 0.01 percent. Below this concentration, the measured area per mg decreased with increased concentration, and, moreover, it was necessary at times to wait several hours before all of the protein was adsorbed on the surface.

When forming films of various proteins, starting with aqueous solutions according to the method that the writer has described elsewhere,[5] the spreading takes place very rapidly and, like Mitchell, he has noted that it is necessary to operate with sufficiently dilute solutions. In this case the results are reproducible, and I have found similar surface concentrations for proteins as different as myosin, amandin, edestin, serum albumin and egg albumin, these being of the order of 0.8 to 1 sq. m per mg under a pressure of 1 dyne per cm.

When all the conditions that must be taken account of in order to secure a perfect spreading are satisfied, it appears that the *isotherms obtained with the most diverse proteins are almost identical.* Figure 1 shows the general form of these isotherms. It is to be remarked that, although the upper parts of these curves remain similar, the lower parts undergo a displacement towards greater areas when the *p*H of the sub-

[1] Joly, Comptes rendus **208**, 975 (1939); J. Chim. Phys. **36**, 285 (1939).
[2] J. Guastalla, Comptes rendus **208**, 1078 (1939).
[3] D. G. Dervichian, Comptes rendus **209**, 16 (1939).
[4] J. S. Mitchell, Trans. Faraday Soc. **33**, 1129 (1939).
[5] D. G. Dervichian, Nature **144**, 629 (1939).

strate deviates in either direction from the isoelectric point. Adam and Miller[6] have demonstrated the existence of a similar phenomenon with fatty acids on an alkaline substrate, and with amines on an acid substrate. The expansion of the layer is due in these cases to the ionization of polar groups which therefore repel each other. It can thus be asserted that protein films behave like a mixed layer of fatty acids and amines, and that the polar groups are in contact with water as in monomolecular layers.

Neurath and Bull[7] in particular have insisted on the fact that the conditions of space required are exactly such as to provide for an assembly with an alternating arrangement, that is to say, with lateral chains alternately polar and non-polar directed, according to circumstances, toward the top or the bottom of the polypeptide chain.

In regions of high pressure where the film commences to collapse, the area per mg of protein is of the order of 0.5 to 0.6 sq. m. The area that may be attributed to a single amino acid residue

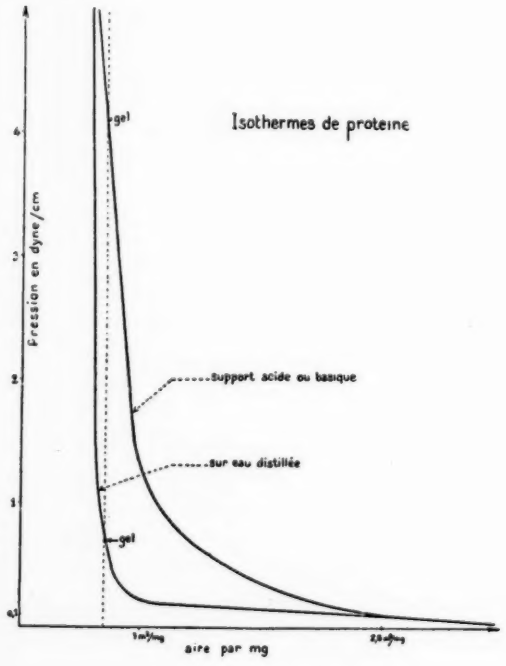

FIG. 1.

of mean molecular weight 120 may be calculated to be 10 to 12A². But chemical analysis of proteins gives in general the proportion of one polar residue to one non-polar.* If it is supposed that each of these categories is oriented either towards the upper surface or the lower surface of the layer, the area that can be attributed to each face per lateral chain would be 2×10 or 2×12, that is 20 or 24A². This value is of exactly the order of magnitude of the space occupied per chain that is found in condensed layers of fatty substances. The building-up of multilayers by the method of Blodgett and Langmuir is made in this region of concentration. By forming a very large number of monolayers of egg albumin, Astbury, Bell, Gorter, and van Ormondt[8] have determined the thickness of a single layer. This is approximately 9.5A and corresponds well with twice the average length of an amino acid side chain. It is thus possible to say that, at least in regions of high pressure, the disposition of the various elements of the protein in the film is as follows: A primary stratum formed by the lateral polar chains oriented in contact with water; then a layer formed of the aggregate of the polypeptide chains; then, immediately above this network, the non-polar lateral chains oriented towards the air. X-ray analysis of the multilayers shows that, in the region of high concentration, the protein is not only denatured but is transformed into a kind of beta-keratin.

It is necessary to insist that there is no limiting area to the extension of proteins on the surface of water. By using an arrangement sensitive to 0.001 dyne per cm, Guastalla[2, 9] has been able to obtain extensions greater than 50 sq. m per mg at pressures of the order of 0.002 to 0.003 dyne per cm. It can thus be affirmed that the layer, under these conditions, is entirely gaseous and that particles exist on the surface of which the

[6] Adam and Miller, Proc. Roy. Soc. **A126**, 526 (1930); **A142**, 401 (1933).

[7] Neurath and Bull, Chem. Rev. **23**, 391 (1938); J. Phys. Chem. **44**, 296 (1940).

* Editorial note: This statement is probably meant by the author to indicate only the order of magnitude. Analytical data for the amino acids derived from a series of proteins gives a ratio of polar to non-polar groups that varies from roughly 0.5 for zein to nearly 2 for gliadin. However, the author fails to appreciate that the dicarboxylic amino acids are present in the intact protein molecule very largely as amides and the side chains of these accordingly contribute little to the polarity of the molecule.—The Editors.

[8] Astbury, Bell, Gorter, and van Ormondt, Nature **142**, 33 (1939).

[9] J. Guastalla, Comptes rendus **206**, 993 (1928).

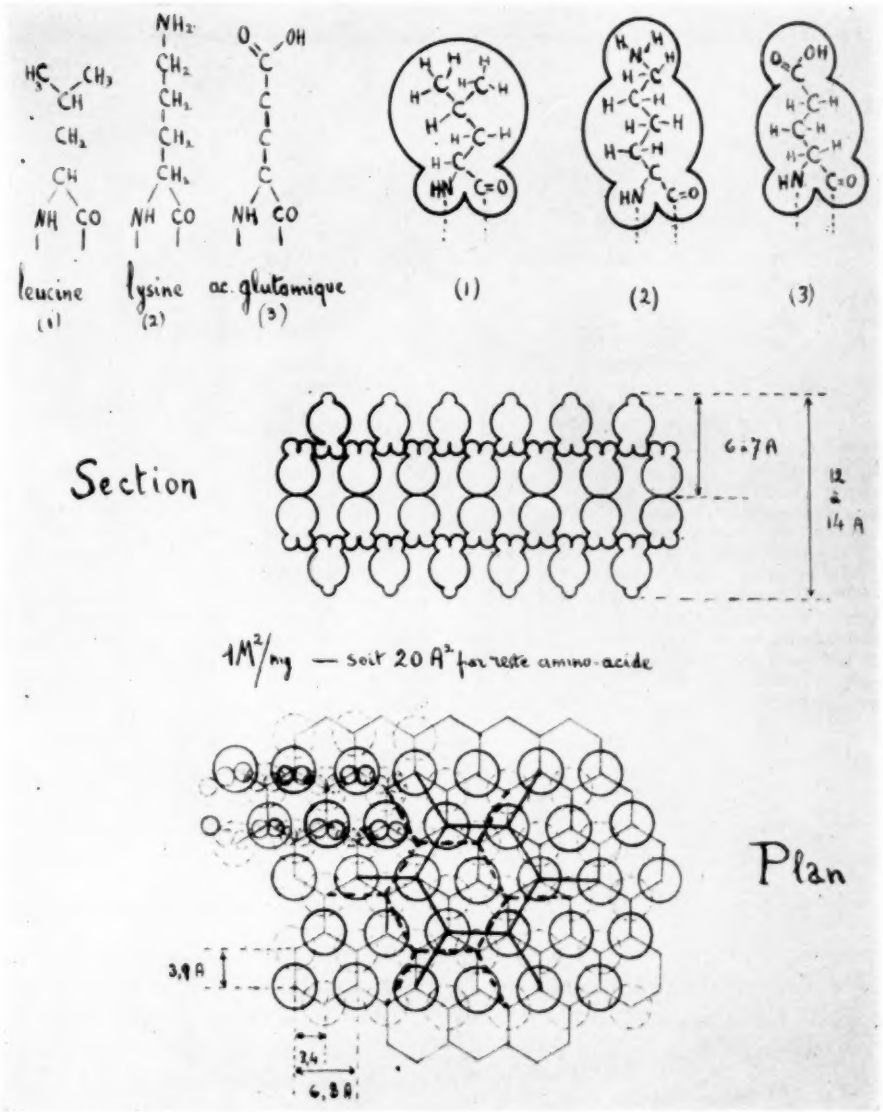

FIG. 2.

molecular weight is of the same order of magnitude as those of Svedberg. But as the writer has shown,[10] there is a very close correlation between the three-dimensional molecular dimensions and the points of transformation in the monomolecular layer. It would be of interest to know the nature of the structure of the layer at the beginning of the region of pressure where it is entirely condensed, that is to say at an area of about 1 sq. m per mg. By supposing that the lateral chains have the same orientation as in the preceding case, one finds, for this concentration, a mean area of 20A² per amino acid or of 40A² per lateral chain in each face of the layer. This area is very close to the 38 and 39A² that is found for the molecular space required for a fatty substance at the extreme limit of the state that I have called "*mésomorphe dilaté*," immediately before the appearance of the liquid isotrope. It would be hazardous to draw a conclusion from this; all that may be said is that, provided they possess free rotation, the chains are still clearly

[10] D. G. Dervichian, J. Chem. Phys. **7**, 931 (1939).

TABLE I. Dimensions of protein molecules on the assumption that these are elongated ellipsoids.

Protein	f/f_0	b/a	M	petit axe $2a$	grand axe $2b$	Produits de diss $2a$	$2b$
Myoglobine	1,11	3,1	17.200	16,5Å	51Å		
Lactalbumine	1,16	3,9	17.400	14	55		
Erythrocruorine (Lampetra)	1,16	3,9	18.100	14,2	55		
Protéine du B. Phlei	1,22	4,9	17.000	12	59		
Protéine du B. de la Tuberculose (Homme)	1,25	5,4	32.000	13,8	75		
Protéine de Bence-Jones β	1,31	6,9	37.700	12,5	86		
Crotoxine	1,22	4,9	30.000	14,2	70		
Hémoglobine: produit de dissociation	1,20	4,5	39.000	16,7	75		
Insuline (oxydée)	1,27	5,9	43.300	14,3	85		
Lactoglobuline	1,26	5,6	40.000	14,7	82		
Concanavaline B	1,25	5,4	42.000	15,1	82		
Ovalbumine	1,16	3,9	42.000	18,7	74		
Sérum-albumine (Cheval)	1,27	5,9	69.000	16,8	100		
Concanavaline A	1,26	5,7	96.000	19	108		
Canavaline	1,31	6,85	113.000	17,8	122		
Sérum-globuline (Cheval)	1,44	9,6	158.000	16,1	155		
Sérum-globuline (Homme)	1,49	10,8	176.000	15,5	167		
Sérum-globuline anti-pneumo. (Lapin)	1,52	11,5	158.000	14,3	165		
Sérum-globuline anti-pneumo. (Homme)	1,53	11,8	195.000	15	177		
Phycocyanine: produit de dissociation	1,38	8,2	138.000	17,1	140		
Hémocyanine (Eledone Moscata): prod. de diss.	1,93	25,9	460.000	12	310		
Hémocyanine(Helix Pomatia): prod. de diss.	1,81	20,9	500.000	14	293		
Hémocyanine (Helix Pomatia): prod. de diss.	1,74	17,7	760.000	17,9	316		
Hémocyanine (Helix Nemoralis): prod. de diss.	1,80	20,5	800.000	16,6	340		
Sérum-globuline anti-pneumo (Cheval)	1,86	23,8	910.000	15,5	370		
Sérum-globuline anti-pneumo (Vache)	1,98	28,2	910.000	13,8	390		
Sérum-globuline anti-pneumo (Porc)	2,02	29,2	910.000	13,6	397		
Sérum-globuline (Lampetra)	1,41	8,9	360.000	22,3	200		
Exelsine	1,13	3,4	295.000	39,5	134		
Edestine	1,21	4,8	310.000	32	152		
Amandine	1,28	6,2	330.000	27,8	171		
Prolamines							
Gliadine	1,60	13,9	27.300	6,9	96		
Hordéine	1,64	14,2	27.500	6,9	98		
Zéine	2,4	52	40.000	3,2	166		

closer together than in the true liquid state where one finds areas of 50 to 60A² per chain. If a density of about 1.3 is assumed, the thickness of the protein layer in this region would be about 7.5A.

SOAP MICELLE AND PROTEIN MOLECULE

It appears that the globular protein molecule, in a manner analogous to that of the soap micelle, when in solution conceals its non-polar parts in the interior whilst it turns the greatest possible number of polar groups towards the water. From this point of view it is possible to assert that the globular particle and the monolayer are identical: both are equally hydrated at the surface of contact with water and, if one considers the expanded molecule as forming part of the surface of a globule of infinitely large radius of curvature, one can consider the face turned towards the air as its interior and still maintain that it conceals its hydrophobic parts in the interior.

In the case of the protein molecule in solution, the best manner to realize these conditions consists in superposing two films in such a way as to conceal their hydrophobic faces by applying them one against the other and turning the two hydrophilic faces towards the exterior (Fig. 2).

In a thesis published at Amsterdam in 1936, Philippi[11] had already arrived at most of the conclusions just expressed. This theory of Philippi seems to have been entirely disregarded.[12]

[11] G. T. Philippi, *On the Nature of Proteins* (N.V. Noord-Hollandsche Uitgeversmaatschappij, Amsterdam, 1936) p. 106.

[12] In order to describe the disposition of the elements of the layer on three superposed planes, Philippi has made use of the expression "triplex films" in analogy to the expression "duplex film" introduced by Langmuir. Unfortunately, the notion of a duplex film having been utilized in a different sense, it seems that Philippi's idea has been incorrectly interpreted. See I. Langmuir, "Protein Monolayers," *Cold Spring Harbor Symposia* (1938), Vol. 6, p. 181.

TABLE I.—*Continued.*

Protein	f/f_0	b/a	M	petit axe $2a$	grand axe $2b$	Produits de diss $2a$	$2b$
Protéines complexes et Ferments							
Insuline	1,13	3,4	38.000	20Å	68Å		
Thyroglobuline (Porc)	1,43	9,3	640.000	26	240		
Pepsine	1,08	2,6	37.500	24	60		
Ferment jaune	1,17	4,1	80.000	22,5	92		
Catalase	1,25	5,4	250.000	27,5	148		
Uréase	1,19	4,4	480.000	39	170		
Chromo-protéines							
Hémoglobine (Homme)	1,16	3,9	63.000	21,6	85		
Hémoglobine (Cheval)	1,24	5,3	68.000	18,2	97	(16,8)	(76)
Cytochrome C	1,29	6,15	15.600	9,8	60		
Phycocyanine	1,22	4,9	273.000	30	147	(17,1)	(140)
Phycoérythrine	1,21	4,7	290.000	31,5	148		
Hémocyanine (Pandulus)	1,07	2,3	400.000	57	130		
Hémocyanine (Palinarus)	1,23	5,1	450.000	34,8	176		
Hémocyanine (Homarus)	1,27	5,8	780.000	38	220		
Hémocyanine (Nephrops)	1,23	5,1	820.000	42,5	215		
Hémocyanine (Calocaris)	1,22	4,9	1,330.000	51	250		
Hémocyanine (Eledone Moscata)	1,39	8,4	2,800.000	45,5	385	(12)	(310)
Hémocyanine (Octopus)	1,38	8,2	2,800.000	46,5	380		
Hémocyanine (Rossia)	1,36	7,7	3,300.000	51	395		
Hémocyanine (Helix Pomatia)	1,24	5,3	6,650.000	83	440	(14)(17,9)–(293)	(316)
Hémocyanine (Helix Nemoralis)	1,24	5,3	6,500.000	83	440	(16,6)	(340)
Hémocyanine (Busycon)	1,23	5,1	6,800.000	86	440		
Erythrocruorine (Chironomus)	1,63	14,8	31.500	7	104		
Erythrocruorine (Lampetra)	1,16	3,9	18.100	14	55		
Erythrocruorine (Planorbis)	1,39	8,4	1,580.000	39,5	328		
Erythrocruorine (Lumbricus)	1,21	4,8	3,050.000	69	330		
Erythrocruorine (Arenicola)	1,25	5,4	3,000.000	61	330		

The disposition in a double layer is the more plausible since this has been recently demonstrated to be the constitution of soap micelle. According to results obtained by x-ray analysis of solutions of soap of different concentrations made by Stauff [13] and by Kiessig and Philippoff,[14] it is evident that the micelle is not formed of a more or less spherical swarm of molecules, but by the superposition of two monomolecular layers. The molecules are disposed in double layers almost as in the crystals of fatty acids with the difference that only a single value of about 4.6A for the side spacing is found, the molecule being probably free to turn around its axis, and the structure being that of a liquid crystal (*état smectique*). The large spacing increases regularly with dilution. Even though the paraffin extremities are placed face to face, a layer of water is interposed between polar groups. In proportion as the solution is diluted this layer of water continues to thicken. The "large micelles" of McBain are formed by a certain number of layers thus superposed. The "ionic micelle" of Hartley should represent a single one of these double layer elements.

In their general disposition, the protein molecules of Svedberg should be similar to the elementary micelles of solutions of soap.

FORM AND DIMENSIONS OF PROTEIN MOLECULES

In agreement with Lawrence,[15] it may be supposed that, in the case of soaps, the dimensions of the small micelles (that is to say the number of constituent chains in each layer) should depend only on the equilibrium between the parts of the heteropolar molecule. On the other hand, in the case of proteins, the different side chains are packed together and belong to the same mole-

[13] Stauff, Kolloid Zeits. **89**, 224 (1939).
[14] Kiessig and Philippoff, Naturwiss. **27**, 593 (1939).
[15] A. S. C. Lawrence, Trans. Faraday Soc. **31**, 192 (1935).

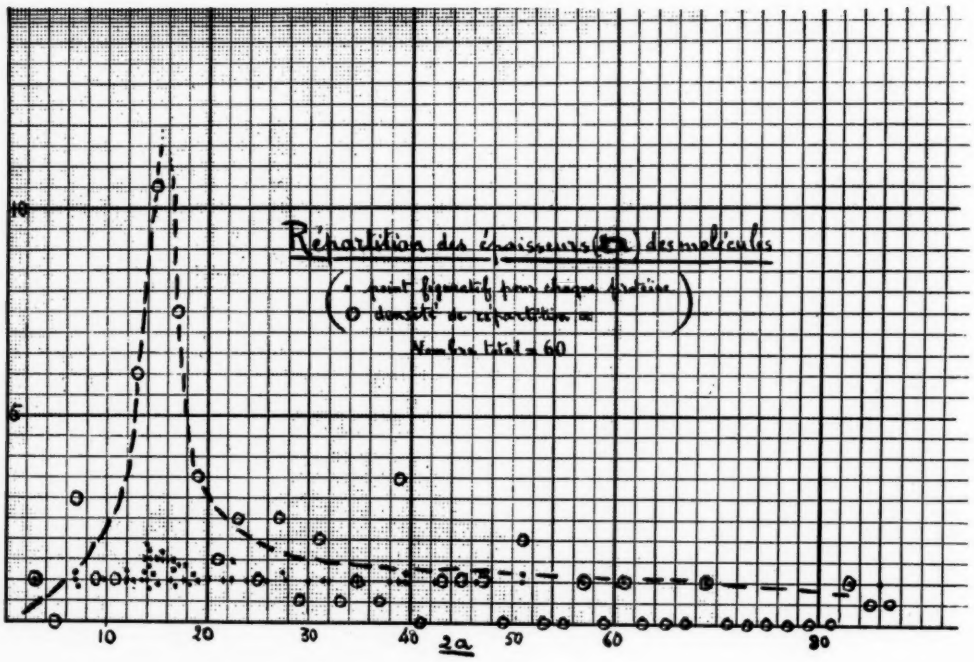

FIG. 3.

cule, and the dimensions of the micelle are fixed by the molecular weight. The thickness of the micelle remains almost constant and equal to twice that of a monolayer on the surface of water. For the reasons already expressed above, we may adopt as a mean value the thickness per layer that corresponds to a surface concentration of 1 mg per sq. m, that is 7.5A. This gives about 15A for the double layer. The molecular weight being known, one can calculate the number of amino acids contained in each layer and accordingly, by multiplying by $20A^2$, the area of the faces. For a molecule of molecular weight 17,500 (myoglobin or lactalbumin) one finds $1450A^2$, and a diameter of about 45A. The thickness of this flattened molecule being constant (15A), the diameter should vary with the square root of the molecular weight; for example, it should be 70A for egg albumin (42,000) and 140 for serum globulin (176,000).

It is interesting to see to what extent this hypothesis of flat disk-like molecules is compatible with the experimental results on the dissymmetry of protein molecules.

Neurath[16] and Polson[17] have independently calculated the dimensions of protein molecules on the assumption that these are elongated ellipsoids. They have made use of the dissymmetry constant f/f_0 of Svedberg and Sjögren obtained from measurements of sedimentation and diffusion. The relationship between this dissymmetry constant and the ellipticity of the particles can be deduced from calculations on the diffusion of ellipsoidal particles made by Herzog, Illig, and Kudar[18] on the one hand, and Perrin[19] on the other. From f/f_0 the ratio b/a of the axes of the ellipsoid of revolution can be deduced. Knowing the ratio of b/a and the molecular volume calculated from the molecular weight, it is simple to calculate the respective dimensions of the two axes a and b. With the hypothesis of elongated molecules, one finds values of a and b from which it is difficult to draw a clear conclusion.

If the molecules are disk-shaped, it is necessary, on the contrary, to carry out the calculation as if they were *oblate* ellipsoids. Table I contains the values of the a axis of revolution and of b, calculated according to this hypothesis, for all

[16] H. Neurath, J. Am. Chem. Soc. **61**, 1843 (1939).
[17] A. Polson, Kolloid Zeits. **88**, 51 (1939).
[18] Herzog, Illig, and Kudar, Zeits. f. physik. Chemie **167**, 330 (1933).
[19] F. Perrin, J. de phys. et rad. **7**, 1 (1936).

the proteins for which the dissymmetry constant is known. It is clear that, for the great majority, the thickness a lies between the limits 12 and 18A, that is to say close to the value of 15A that we have already noted. It should not be lost sight of that f/f_0 is not known with great precision and that one is making an approximation when a disk is regarded as an oblate ellipsoid.*

The curve in Fig. 3, in which the data of the table are plotted, shows the distribution of the number of molecules that have a given value for a. There is clearly a very sharp maximum in the vicinity of 15A. The large axis evidently varies with the molecular weight giving values close to those anticipated.

The proteins for which the thickness departs very clearly from the mean value of 15A can be classified in two groups. In the first are a number of chromoproteins which form a case to be examined more closely below; secondly, there are certain proteins which have properties that distinguish them from ordinary proteins; for example, the prolamines, which are the only proteins soluble in alcohol, and proteins such as insulin and the enzymes† which may be considered to have a special structure. The prolamines show a thickness comparable to and even less than that of a single monolayer; this may have some relation with their solubility in alcohol, or it may be that treatment with this solvent has transformed them into a fibrous form in which case it is necessary to consider them as elongated ellipsoids and to describe them in terms of the figures of Neurath. Cytochrome may perhaps belong in the same group. It seems certain that conjugated proteins and enzymes possess a structure different from that of ordinary proteins if only because of the presence of a prosthetic group. The case perhaps has much in common with that of the chromoproteins.

For the chromoproteins, and in particular hemocyanin, the interpretation is far more easy and may even throw some light on their mode of formation and their tendency to dissociation. Even though the undissociated molecules may show thicknesses that at times exceed 80A, the products of their dissociation show normal thickness. Furthermore, for most of these products of dissociation, the large diameter is not very different from that of the initial micelle. It behaves as if the large micelle of hemocyanin were formed of a pile of elementary micellar plates, and that the phenomenon of dissociation consists in the separation of these superposed disks. The micelle of hemocyanin would thus be analogous to the large micelle of soaps of Stauff [13] with the difference that the elementary disks are not separated from each other by layers of water but are connected perhaps by the chromatic part.

INTERNAL ARCHITECTURE OF THE MOLECULE

Let us consider a single layer of which the micelle is formed and of this one of its faces, for example, the face in which the polar lateral chains are oriented. These chains of different kinds (aspartic acid, lysine, glutamic acid, arginine, etc.) form a sort of mixed layer and should be studied as a whole from this point of view.

Schulman and Rideal[20] have submitted evidence of molecular interactions in the interior of monomolecular layers. In particular a soluble substance—and one therefore incapable of giving by itself a stable film—when it is injected into the substrate on which the normal layer is

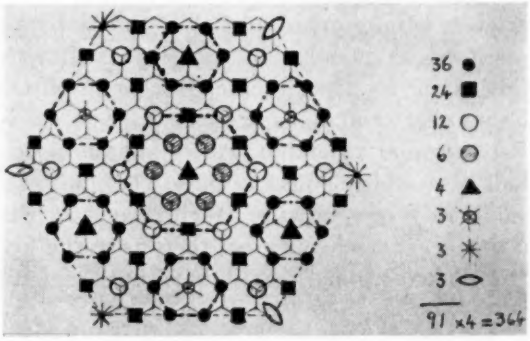

FIG. 4.

* Editorial note: The author neglects to consider data from other sources which indicate that hydration makes an appreciable contribution to the magnitude of f/f_0; see, for example, G. A. Adair, Proc. Roy. Soc. **127B**, 18 (1939), nor does he take account of studies of the relaxation time of protein molecules from dielectric dispersion and double refraction of flow experiments (J. L. Oncley, Ann. N. Y. Acad. Sci. **41**, 121 (1941)).—The Editors.

† Editorial note: The author here refers to "*proteines conjuguées, telles que l'insuline et les ferments.*" Although such enzymes as catalase probably are conjugated proteins, there is no evidence that insulin and pepsin, for example, belong in this class.—The Editors.

[20] Schulman and Rideal, Proc. Roy. Soc. **B122**, 29, 46 (1937).

formed, can be adsorbed upon it, or penetrate it, and form with it a stable mixed layer. Under the same conditions Schulman and Stenhagen[21] have clearly shown the formation of complexes between two different molecular species in the stoichiometric relations of 1 : 1, 1 : 2, and 1 : 3. Such substances as cetyl alcohol and sodium cetyl sulfonate, especially in the presence of water, cannot yield compounds in the chemical sense of the word. The stability of the mixed layer is far greater than that of the insoluble substance alone. In a paper by Cockbain and Schulman[22] there is a table of different modes of interaction according to the nature of the chains and the polar groups. Schulman and Cockbain[23] have extended this study to the case of emulsions. It is evident, from their experiments, that the most stable micelles are obtained by utilizing, in the formation of the emulsion, the same pairs of substances as those which give complexes in monomolecular layers on the surface of water.

If, in place of only two constituents, we envisage a dozen or twenty, we have conditions such as those that occur during the synthesis of a protein on a surface. In this mixed crystal, the chains, being of different nature, do not have a common plan of symmetry and an assemblage can only be formed which follows an hexagonal symmetry, which is the only compact assemblage possible for a number of cylinders of revolution.

Figure 4 represents a model of a possible assembly for 8 different kinds of lateral chains. In a manner analogous to that observed in an alloy, there is superposed on the element of the mesh a superstructure characteristic of each kind of molecule or molecular group. This superstructure can itself have only an hexagonal symmetry. This symmetry thus imposes the condition that the number of amino acids of one given species that surround an amino acid of another species shall be a multiple of 2 or of 3. The number of amino acids of each kind which occur according to this general scheme must then be of the form $2^n \cdot 3^m$. We recognize here the rule that Bergmann and Niemann have established by means of chemical analysis.[24]

Each layer of the molecule forms the smallest element with hexagonal symmetry that can be established when different amino acids are associated in variable proportions but with restrictions in the choice of numbers to the series of the form $2^n \cdot 3^m$. One can thus easily conceive that it is not possible to remove a single amino acid from the network without destruction of the entire edifice, or at least without the total number of constituents, and therefore the molecular weight, changing suddenly to a new value corresponding to a new distribution.

It is necessary to point out that the structure of the molecule is imposed by the packing of the lateral chains; these are oriented and maintained in position by Van der Waals forces as the chains of different molecules are maintained in a monomolecular layer or in the soap micelle. This compact assembly of the lateral chains (in the manner of a bundle of asparagus) imposes the hexagonal symmetry and brings about the disposition in layers. There is no doubt that the peptide bond forms the linkage between the different amino acids, but the polypeptide chain is forced to adapt itself to this arrangement and is therefore very likely in a state of constraint; perhaps it may thus form the loops that Astbury has imagined to explain the structure of α-keratin. In the theory of Wrinch[25] it is, on the contrary, the polypeptide chain which is the fundamental element: this is folded, following certain regular hexagonal contours, with the hypothetical formation of diketopiperazine rings.* Another difference is that, in the theory of Wrinch, there is no concern, properly speaking, with an hexagonal network in the crystallographic sense, since certain hexagonal contours are not in contact. It should not be impossible to reconcile certain

[21] Schulman and Stenhagen, Proc. Roy. Soc. **B126**, 126 (1938).
[22] Cockbain and Schulman, Trans. Faraday Soc. **35**, 725 (1939).
[23] Schulman and Cockbain, Trans. Faraday Soc. **36**, 651 (1940).
[24] Bergmann and Niemann, J. Biol. Chem. **115**, 77 (1936); **118**, 301 (1937).
[25] D. Wrinch, Proc. Roy. Soc. **A160**, 59 (1937); **161**, 505 (1937).

* Editorial note: This is scarcely a clear statement of the speculation of Wrinch. The fundamental assumption from which Wrinch develops her fabrics is that intramolecular changes take place as a result of which each amino acid unit is combined to its neighbors by four linkages instead of two as in the simple polypeptide chain. The logical mathematical development of this view leads to a two-dimensional fabric, the outstanding characteristic of which is the cyclol ring which has little in common with the diketopiperazine ring.—The Editors.

points in the two theories: Wrinch likewise starts with a plane model and by joining the positions of the lateral chains on her figures, these are found to be disposed at the apexes of an hexagonal network. However, in the present theory, no hypothesis is made with regard to new chemical structure (diketopiperazine rings or lactam-lactim transformations), and the whole structure is imposed simply by the necessities of organization and of symmetry. Finally, Wrinch constructs her molecule in the form of a hollow cage developed from the plane surfaces, and it is upon this last point that the two theories are irreconcilable.[26]

X-Ray Diffraction†

The structure proposed here seems to be in agreement with the Patterson diagram obtained by x-ray analysis of insulin by D. Crowfoot.[27] The model in Fig. 4 of the present article has been suggested by the diagram of Crowfoot. In analyzing the results of Crowfoot, Bernal indicates that there are concentrations of scattering material at distances of the order of 10A and on the other hand prominent internal distances of about 4A. It is a question here of a crystal, not of a molecule in solution, and it is therefore necessary to anticipate that the lateral chains should be in a state corresponding to a very condensed film. The first interval of 10A should correspond to the thickness of the elementary layer, and that of 4A to the mean distance between amino acids in the plane of the elementary hexagons.

In the lower part of Fig. 2, the solid circles represent the lateral chains directed towards the upper surface of the elementary layer, while the dotted circles represent the lateral chains directed towards the lower surface. The complete set of lateral chains, directed alternately towards the upper and lower surfaces, is thus arranged at the apexes of a small hexagonal network. But it is each of these two categories of chains—polar or non-polar—which forms the fundamental mesh of the centered hexagon. It is apparent that the two large networks (solid and dotted lines) thus formed are not directly superposed the one on the other. Midway between these two networks the connections between the amino groups and carboxyl groups, which form the polypeptide chains, are located. The groups which form this chain are shaded in the figure.

DENATURATION

We shall admit, with Astbury and his collaborators,[28] that denaturation is only the first stage in the transformation of the protein structure from its native condition into a fibrous phase, and that it implies the liberation or formation of polypeptide chains. We have seen that, under the orienting action of water, the peptide linkages undergo a certain constraint and that the whole structure is in a metastable state. Elevation of temperature or dehydration can destroy this orientation. Denaturation would thus only be a passage from a metastable state in the form of a layer to a fibrous form in which the preponderating element is, as in the keratins, the polypeptide chain. In accord with measurements of the heat of denaturation,[29] the energy required for such a polymorphic transformation need be only small. Once the primitive arrangement breaks, it is practically impossible for the filamentous particles to be reassembled in such a way that the lateral chains shall regain their order in their hexagonal symmetry. In short, the entropy of the denatured protein is greater than that of the native protein.[30] If the analogy with liquid crystals is followed out, one would say that the denatured protein passes through a stage that may be regarded as fibrous (*l'état nématique*).

ELECTROKINETIC MOBILITY

The observed identity between the mobility of quartz particles covered with protein and that

[26] For an analysis and criticism of Wrinch's theory see L. Pauling and C. Niemann, J. Am. Chem. Soc. **61**, 1860 (1939). [Wrinch's rebuttal of Pauling and Niemann's criticism is to be found in J. Am. Chem. Soc. **63**, 330 (1941).—The Editors.]

† Editorial note: This discussion of the relationship of x-ray diffraction observations to the author's speculation is based upon views and formal analogies for which there is, in fact, little experimental evidence.—The Editors.

[27] J. D. Bernal, Proc. Roy. Soc. **A170**, 76 (1939).

[28] Astbury and Lomax, Nature **133**, 795 (1934); Astbury, Dickinson, and Bailey, Biochem. J. **29**, 2351 (1935).

[29] Anson and Mirsky, J. Gen. Physiol. **17**, 393 (1934).

[30] Mirsky, *Cold Spring Harbor Symposium* (1938), Vol. 6, p. 152.

of the molecule itself[31] is to be anticipated when it is admitted that the adsorbed layers are identical with those which form the two flat surfaces of the protein molecule.

HYDRATION, SWELLING, AND CHANGE OF PHASE

It is necessary to regard solutions of proteins as being formed on the same model as that which x-ray analysis has shown to be present in solutions of soaps.[13] At great dilutions, the elementary micelles are independent, but, beginning with a certain concentration (the critical concentration of McBain corresponding to about 20 percent in the case of soaps), the micelles are influenced both by the Coulomb forces of repulsion and by a kind of steric hindrance (the lateral distances between micelles having become of the same order of magnitude as the diameter of the micelles) and can only become piled up. They are accordingly superposed and are separated by layers of water of a definite thickness: the whole congeals into a fixed structure. The solution is always very fluid since there are no forces of cohesion at play and nothing is opposed to shearing in any direction by the slipping of the layers of water. At higher concentrations, the flat molecules are almost side by side and the layer of water becomes very thin. At the limit, a simple calculation shows that a monomolecular layer of water covering the two exterior hydrophilic faces of the molecule represents about 20–25 percent of the total weight, whatever may be the molecular weight of the protein: this is the bound water.

Beginning at the point where layers of water molecules no longer intervene, the phenomena cannot proceed in a continuous fashion; that is to day sudden changes in the properties should be produced according as there is one layer of water the more or less. From this comes the great number of different phases that can be observed during swelling, to say nothing of the phenomena of coacervation.

The decrease in solubility after denaturation becomes explicable since, with the new structure, the hydrophobic groups are no longer concealed.

[31] See, in particular, Abramson, Gorin, and Moyer, Chem. Rev. **24**, 345 (1939).

BIOCHEMICAL PROPERTIES

If two or more molecules become joined by their plane faces, the pile thus obtained, with its top and bottom surfaces free, presents no more ionizable groups than a single one of the elementary micelles, even though the lateral surface is augmented. The combination will thus be less soluble and may precipitate. Such a union is made naturally in the molecule of hemocyanin possibly with the intermediation of the pigment. It may be supposed that, beside the reaction of precipitation, the prosthetic groups of antibodies may play the same role as the chromatic groups of hemocyanins. In any case, the existence of a crystalline structure at the surface of a plane molecule may be easily adapted to the various attempts that have been made to explain the selective character of the phenomena of immunity and of the action of enzymes; furthermore the disappearance of these properties, when the crystalline structure is modified by denaturation, is readily understood.

The formation of complex lipo- or glucoproteins may be regarded in an analogous way either by replacing one of the layers of the protein molecule with a monomolecular layer of lipid or glucoside, or by the simple piling up of a micelle of protein with a micelle of the other substance.

In general, the particles of protein in solution appear to us in a double aspect: by their resemblance to soaps they behave like a *micelle* formed by the assembly of a large number of different molecules which is capable of being split into two flat parts in the process of forming a monolayer; but, on the other hand, the peptide linkages combining several different elements chemically form an individual, a *molecule*. It is remarkable that the linkages are such that they permit different groupings to become oriented and disposed as in the micelle of soap. And this gives rise to the thought that, at the moment of its synthesis, the different parts of the protein molecule have been at first juxtaposed in a micelle or on a surface matrix where, once oriented and arranged, chemical reaction takes place which unites them. This appears to be the more reasonable if there has been, as one is apt to think, an intervention with an intracellular synthesizing enzyme; the action of enzymes, like that of catalyzers, is certainly a surface action.

Letter to the Editor

The Thermal Hydrogen-Oxygen Reaction; Measurements in Large Vessels

O. OLDENBERG AND J. E. MORRIS
Research Laboratory of Physics, Harvard University, Cambridge, Massachusetts,
April 13, 1943

THE theory of the hydrogen-oxygen reaction given by von Elbe and Lewis[1] leads to interesting predictions for the second explosion limit. The chain-breaking effect of the walls is identified with the adsorption on the walls of HO_2 radicals. Thus an *increase of vessel size* should improve the chance for these radicals to continue the chains and so *increase the tendency toward explosion.*

Experiments started several years ago, at present interrupted, are reported here. We compared spherical vessels with volumes of 4l and 1/5l, the former far exceeding the size investigated before. Considering a criticism of von Elbe and Lewis, we observed the second explosion limit as a function of the temperature at temperatures so low that no appreciable water vapor was formed during the unavoidable period of manipulation. Aging has little effect on the 2-explosion limit except that, as reported before, it removes the inhibition period which is noticeable in the steady reaction, not the explosion; thus it favors the formation of H_2O during the manipulation and so indirectly may cause errors. These vessels were used clean or with covers of KCl or $BaCl_2$. In Fig. 1 each point shows the average of several measurements taken in rapid succession to secure uniform surface activity. At 470° in Pyrex and 490° in KCl the various points indicate the reproducibility after many intervening runs at different temperatures.

With KCl the *small* vessel shows a lower 2-explosion limit (less tendency toward explosion), but only so little lower that the effect may well be due to lack of reproducibility when vessels are exchanged. With $BaCl_2$ the change of diameter makes no difference in the 2-explosion limit; the curve common for both sizes (not drawn in Fig. 1) falls between the two KCl curves. As found by von Elbe and Lewis, for clean Pyrex the curves are higher than for these salts; for Pyrex, however, with the *large* vessel there seems to be less tendency toward the explosion; but again the small difference may be insignificant. A comparison of the various measurements fails to show a definite trend with increasing size.[2]

The fact that in KCl the large step to the 4-l vessel has no strong effect on the 2-explosion limit agrees with computations of von Elbe and Lewis, which, however, are based on far-reaching approximations. Furthermore, this fact may be attributed to the comparatively low tempera-

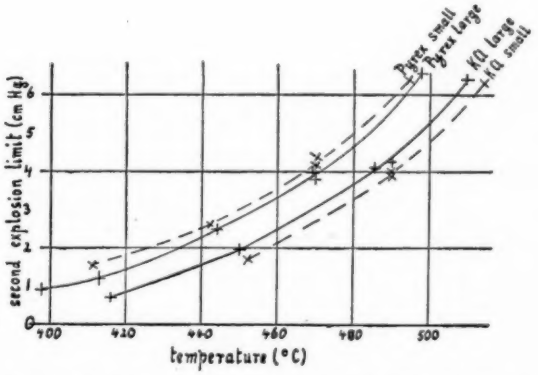

FIG. 1. Effect of vessel size on second explosion limit in Pyrex and KCl (large vessels—solid curves; small vessels—dashed curves). In $BaCl_2$ (not entered in figure) the curves for small and large vessels coincide and are located between the curves for KCl.

tures applied which do not favor certain chain-continuing reactions of the radical HO_2. The fact that the explosion limit in Pyrex is higher than in KCl is in line with the theory assuming more reflections and therefore longer duration of the chains. But it is not easily explained that the increase of the Pyrex vessel to a size as large as 4l fails to show any effect. The theory when applied to Pyrex (chain-breaking efficiency ϵ small, factor B large) seems to predict a substantial increase of the 2-explosion limit without a limiting value being reached for large diameters.

A more thorough comparison of the experiments with the recent theory of von Elbe and Lewis, which is strikingly successful in describing the effects exerted on the 2-explosion limit by the addition of various gases, will be published at a later date.

[1] B. Lewis and G. von Elbe, *Combustion, Flames, and Explosions of Gases* (University Press, Cambridge, 1938); J. Chem. Phys. **10**, 366–393 (1942).

[2] S. Kimata, N. Aomi, and R. Goto [Rev. Phys. Chem. Japan, **15**, 44 (1941)] report results obtained in Pyrex some of which seem to indicate a trend while other results of the same set of measurements contradict the trend.

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CONTENTS

THE JOURNAL OF CHEMICAL PHYSICS Vol. 11, No. 5 MAY, 1943

Sorption of NH_3 on Montmorillonitic Clay . . . . . I. CORNET 217

Raman Spectra of Hydrocarbons. II. 2-Methyl-1-Heptene and 6-Methyl-1-Heptene . . . . . FORREST F. CLEVELAND 227

Infra-Red and Raman Spectra of Polyatomic Molecules. XIX. Acetaldehyde and Acetaldehyde-d_1 . . . . . J. CARRELL MORRIS 230

Structure of the Protein Molecule . . . . . D. G. DERVICHIAN 236

Letter to the Editor:

Thermal Hydrogen-Oxygen Reaction: Measurements in Large Vessels . . . . . O. OLDENBERG AND J. E. MORRIS 247

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